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VOLUME XX | SEPTEMBER 14, 1931 | NUMBER 18


# Saponification Treatments for Cellulose Acetate Rayon

*By* A. J. HALL, B.Sc., F.I.C., F.T.I.


**There seems to be at the present time a reawakened interest in cellulose acetate saponification. The effects of saponification on dyeing with aniline black and S.R.A. dyes are discussed in this article. The effect of saponification on certain special properties such as heat resistance are also discussed together with methods of treatment.**


AT THE present time there appears to be an awakened interest in processes for saponifying cellulose acetate rayon, and there are indications that this interest will eventually bear fruit in the discovery of new technical processes for this type of rayon. Quite a number of recent investigations have shown that the properties of cellulose acetate rayon can be enhanced by judicious saponification—not completely but to a limited extent.

Saponification of cellulose acetate rayon is no new thing. It was practiced early in the manufacture of this rayon because only after this treatment could it be dyed; there was then no knowledge of S.R.A., Dispersol, Celliton, and Duranol colors which could be directly applied to the rayon. But apart from this it must not be forgotten that a saponification process is utilized in the actual manufacture of the rayon. It must be remembered that most of the acetate rayons now available are not composed of cellulose triacetate but of a lower acetate containing from 2½ to 2¾ acetyl groups per molecule of cellulose ($C_6H_{10}O_5$). In order to manufacture these lower acetates it is curiously necessary to prepare first the triacetate and then saponify this to the lower acetate. The following given by H. Stadlinger (Textilberichte, 1930, 11, 450) indicates how the lower acetates are favored by the various cellulose acetate rayon manufacturers:

| *Type of Rayon* | *Acetyl Content* |
|---|---|
| Setilose (Belgian) ..... | 53.2% |
| Celanese (English) ..... | 53.8 |
| Rhodiaseta (French) ..... | 54.4 |
| Rhodiaseta (German) ..... | 54.3 |
| Aceta (German) ..... | 54.9 |

The above acetyl contents were obtained by immersing the rayon in cold N/2 alcoholic caustic potash for 48 hours and then back-titrating the excess of alkali; and they should be compared with the acetyl content of the triacetate which is 62.5%.

Generally this operation by which cellulose triacetate is converted into a lower acetate is termed *hydrolysis* rather than saponification, but the chemical reaction involved under this term is the same, that is, elimination of acetyl groups. The term hydrolysis is most probably employed because the splitting-off of acetyl groups is brought about by the action of dilute acid; saponification of fully formed cellulose acetate is almost always effected by treatment with an alkali.

## Saponification

The saponification of cellulose acetate rayon is most conveniently effected by use of a caustic alkali such as caustic soda or potash; sodium and potassium carbonates are much less useful. Ammonia appears to be quite unable to effect saponification. Saponification is a process in which each rayon filament is attacked from the outside; the rate of saponification is thus intimately dependent on the surface area of each filament exposed to the saponifying solution and on the special properties of the saponifying agent. Thus the writer has generally observed that caustic potash appears to saponify more rapidly than caustic soda, and that solutions of calcium hydroxide and barium hydroxide saponify the rayon more regularly than solutions of caustic soda or potash. If during saponification the cellulose acetate rayon is continuously shaken with the alkaline solution then uniform saponification is insured whatever the alkali employed, but if the shaking is intermittent and irregular it is then that the more even saponifying action of the alkaline earth hydroxides becomes apparent.

Until quite recently it has been assumed that the degree of saponification effected is directly proportional to the

amount of alkali neutralized according to the following equation:

$$C_6H_7O_2(O.COCH_3)_3 + 3NaOH = C_6H_{10}O_5 + 3CH_3COONa$$

cellulose triacetate — cellulose

but there is now reason to doubt the accuracy of this assumption in certain instances. For instance, in (E.P. 125153) is described a process for saponifying cellulose acetate rayon by means of alcoholic solutions of caustic soda, it being claimed that under such conditions the saponification is very uniform. Since then the discovery has been made (E.P. 313404) that if alcohols such as glycol and similar polyhydric alcohols are used instead of ethyl alcohol the efficiency of the saponification process is so increased that much more cellulose acetate is saponified than is equivalent to the amount of alkali used. For instance, if cellulose acetate rayon is treated for about sixteen hours at 25° C. with dry ethylene glycol (twenty times the weight of rayon) containing an amount of the sodium alcoholate of this glycol theoretically sufficient to saponify only 7% of the acetate then actually about 50% saponification occurs; this saponification is accompanied by a loss of weight of 19%.

The facts just noted above are very interesting since they open up useful possibilities. As will be indicated later, during saponification there is a tendency for the newly formed cellulose to dissolve in the alkaline liquor when this is moderately concentrated; the properties of the rayon may thus be seriously impaired. But if only a small amount of alkali is required in the saponification then there is much less chance of the cellulose dissolving since the saponifying solution can be quite dilute.

## Aniline Black Processes

A few months ago the writer was interested in the saponification of cellulose acetate rayon materials in connection with processes for dyeing them with Aniline Black. Although the writer and others have succeeded in devising methods for dyeing Aniline Black directly on this type of rayon it must be clearly recognized that there is an alternative method. This alternative consists of first slightly saponifying the rayon with an alkali and then dyeing it Aniline Black by the methods which are commonly employed for cotton goods. As is well known, the dyeing of cotton with Aniline Black is now firmly established and methods are known by which excellent black shades can be regularly produced with little, if any, tendering. These methods are useless when applied to cellulose acetate rayon and in modifying them to render them suitable the process becomes much more costly and difficult to carry out. When all factors are taken into consideration it will be found that it is cheaper to saponify first and then dye Aniline Black by the usual methods. If this method is adopted then the question arises—"Does the saponification process deleteriously affect the rayon?" To answer this the writer carried out certain investigations which will here be dealt with.

## Effect of Saponification on Dyeing

In the first place for purposes of Aniline Black dyeing it is not necessary that the rayon should be saponified beyond an amount just sufficient to give the rayon an affinity for direct dyes equal to that of cotton. This is particularly the case in connection with fabrics consisting of both cotton and cellulose acetate, for if the saponified rayon had a greater dye-absorbing power than the cotton then the Aniline Black dyed fabric would reveal either the cotton greenable (because of insufficient dyeing) and the rayon correctly dyed, or the cotton ungreenable (correctly dyed) and the rayon bronzy (due to excess of dye being present). Generally if a difference exists between the cotton and the saponified rayon it is better for the rayon to have slightly less affinity than the cotton for dyes. From these considerations the necessity arose to ascertain how much saponification was required to give the rayon just the correct degree of affinity for dyes.

In these investigations it was assumed that if the saponified rayon had an affinity for cotton dyes just less than that of cotton then a pleasing uniform shade of black would result in application of Aniline Black—the slightly less depth of color on the rayon would enhance the luster of this fiber. On the other hand, if a dull luster finish was desired then the rayon should be saponified so that it dyed somewhat heavier than the cotton. The necessary degree of saponification was determined by the following experiments with cellulose acetate yarn:

Portions of yarn were steeped at 50° C. for two hours in a weak solution of barium hydroxide of increasing concentration; after this period the solutions were allowed to gradually cool during 17 hours. The alkali contents of the solutions before and after the saponification which thus occurred were determined and from the losses of alkali the degrees of saponification were calculated. Barium hydroxide was employed for the saponification because this alkali was found to produce the most evenly saponified rayon.

The resulting saponified yarns were then dyed together with ordinary cotton yarn with Chlorazol Fast Red K from a bath containing 1/5% of soap and ammonia. The dyeing thus obtained were graded as follows:—

Table I

| *Degree of Saponification* | *Depth of Dyeing* |
|---|---|
| 0.0% | 0 |
| 0.4 | 0 |
| 0.7 | 0 |
| 3.9 | 1 |
| 7.0 | 1 |
| 9.8 | 2 |
| 12.4 | 3 |
| 12.7 | 4 |
| 22.6 | 5 |
| 31.5 | 6 |
| 48.0 | 7 |
| 59.5 | 8 |
| 68.4 | 9 |
| 87.0 | 10 |
| Cotton yarn. | 2 |

0 = lowest depth of shade. 10 = highest depth of shade.

The above results show that after saponification to the extent of about 10% cellulose acetate rayon has an affinity for direct dyes equal to that of cotton yarn. Of course this statement will not be true for all types of cotton yarn since different yarns have their own characteristic affinities for direct dyes. The important fact emerges however that quite a small amount of saponification is required to give cellulose acetate rayon a useful affinity for direct dyes.

Following the above results cotton-cellulose acetate rayon fabric was saponified on a large scale and dyed with Aniline Black; the resulting shade was excellent in every way, and the cost of the process comparatively cheap.

It will be noticed from Table I that under the conditions of saponification employed the affinity of the rayon for direct dyes gradually increases with increase of saponification up to about 90%. This does not agree with some recent results obtained by Coltof, Waterman, and Wolf (Zeit. angew. Chem., 1931, *44*, 166), but it is to be pointed out that in these researches the method of saponification was carried out in a different manner and with a different saponification agent (caustic soda). Coltof, Waterman, and Wolf correlate the affinity for direct dyes of the saponified rayon with the loss of weight produced in saponification as shown in Fig. 1. From this it must

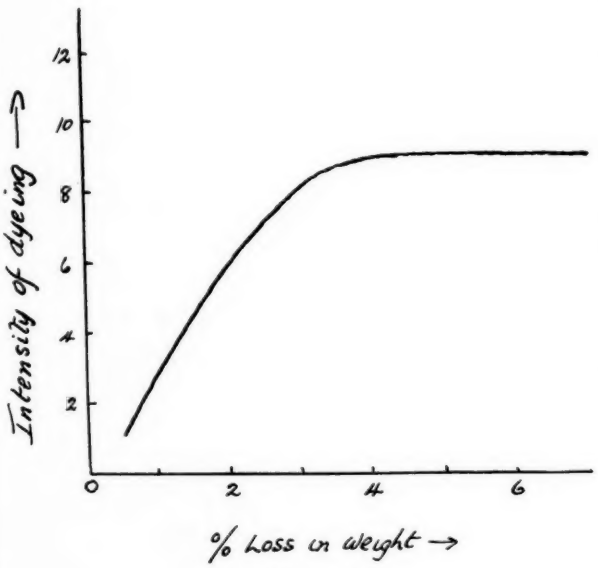



*Fig.* 1

be concluded that the affinity for direct dyes does not increase beyond a point when the loss of weight is equal to about 4%. Since the loss of weight is approximately only one-half the degree of saponification it would thus appear that when 8% of the acteyl content of cellulose acetate has been saponified then the rayon has attained its maximum affinity for direct dyes. Without further knowledge it is difficult to bring these results into agreement but the experience of the writer is quite against such evidence. At the same time it must be remembered that the manner in which the saponification is effected can have a large influence on the reactivity of the regenerated cellulose, and this of course includes its reactivity towards dyes. The more sponge-like the regenerated cellulose the greater its affinity for direct dyes. Thus, if the saponification is carried out in an alkaline solution which also exerts a swelling effect on cellulose then the saponified rayon will have a large affinity for dyes. On the other hand, if the saponified rayon is dried rapidly at a high temperature then its affinity for dyes will be comparatively small.

As might be expected, saponification of a cellulose acetate rayon fiber by, say caustic soda, must proceed inwards from the outside. Thus in a partially saponified fiber the outer layers consist of regenerated cellulose whilst the inner core consists of unchanged cellulose acetate. At intermediate points the degree of saponification increases from the core to the outside. This phenomenon may be easily observed by cutting cross sections of partially saponified rayon which has been afterwards dyed with a direct dye, say Chlorazol Fast Red KS. It will be observed that the depth of coloring decreases inwardly towards the center of the fiber.

### Saponification and S. R. A. Dyes

Just as cellulose acetate rayon gains an affinity for direct dyes when saponified so does it lose its affinity for S.R.A. and other dyes which are commonly used for coloring this type of rayon. The interesting point about this, however, is that saponification must be carried nearly to completion before the rayon quite loses its affinity for S.R.A. dyes. Thus a partially saponified rayon can have an affinity for both direct and S.R.A. dyes. The writer obtained the following results by saponifying Celanese rayon yarns to increasing amounts, then dyeing together with various S.R.A. dyes and comparing the resulting shades:

Table II

| *Degree of Saponification* | *Depth of Shade* | | |
|---|---|---|---|
| | S.R.A. Red VII | S.R.A. Violet II | S.R.A. Blue VII |
| 0.0% | 9 | 10 | 8 |
| 0.4 | 10 | 9 | 9 |
| 0.7 | 10 | 9 | 10 |
| 3.9 | 9 | 9 | 9 |
| 7.0 | 9 | 8 | 9 |
| 9.8 | 9 | 8 | 8 |
| 12.4 | 8 | 7½ | 7 |
| 12.7 | 7 | 7 | 6 |
| 22.6 | 6 | 6½ | 6 |
| 31.5 | 5 | 6 | 6 |
| 48.0 | 4 | 6 | 5 |
| 59.5 | 3 | 3 | 2 |
| 68.4 | 1½ | 2 | stain |
| 87.0 | stain | stain | stain |

0 = lowest depth of shade. 10 = highest depth of shade.

The results also indicate that a very slight degree of saponification appears to increase the affinity of the rayon for S.R.A. dyes.

### Saponification and Heat Deterioration

It is well known that cellulose acetate rayon suffers from the disadvantage that it is not resistant to heat and fabrics containing this rayon are liable to deterioration if ironed with too hot an iron. It is possible to incorporate various substances in the rayon for the purpose of rendering it less easily fusible but much the better method for improving the ironing properties of cellulose acetate rayon is that of partial saponification.

A short while ago the writer (Rayon Record; 1930, *4*, 1301) carried out investigations with the object of discovering exactly how the fusing point of ordinary cellulose acetate rayon was raised by saponification. Celanese yarns were saponified to increasing extents and their fusion points determined. The fusion point of such rayon cannot be ascertained so exactly as say the melting point of an organic chemical because of the slowness with which fusion occurs, but the following was the method adopted:

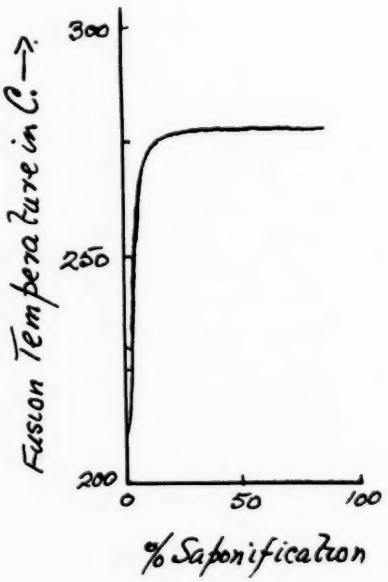



*Fig. 2*

The saponified yarns (saponified to varying degrees) were wound around the bulb of a thermometer which was then placed within a boiling tube and immersed in a hot bath of oil. The temperature was raised in stages of 5 C. and the yarns were exposed to each temperature stage for five minutes. After each exposure the thermometer and attached yarns were withdrawn and the condition of the yarns examined. The point of fusion was considered to be that at which the individual filaments in the yarn just coalesced. In this manner the following results were obtained:

Table III

| *Degree of saponification* | *Temperature of coalescence* |
|---|---|
| 0.0% | 215-220 C. |
| 0.4 | 240-245 |
| 0.7 | 230-235 |
| 3.9 | 250-255 |
| 7.0 | 240-245 |
| 9.8 | 275-280 |
| 12.4 | ditto |
| 12.7 | ditto |
| 22.6 | 265-270 |
| 31.5 | 275-280 |
| 48.0 | ditto |
| 59.5 | ditto |
| 68.4 | ditto |
| 87.0 | ditto |

They indicate very clearly that even a small amount of saponification causes a large improvement in the resistance of the yarn to hot ironing, and the curve in Fig. 2 further shows how saponification in the early stages is even more beneficial than in the later stages.

Thus the utility of cellulose acetate rayon materials can be much improved by slight saponification.

### Method of Saponification

From the practical point of view it may be asked which is the best method for effecting saponification since there

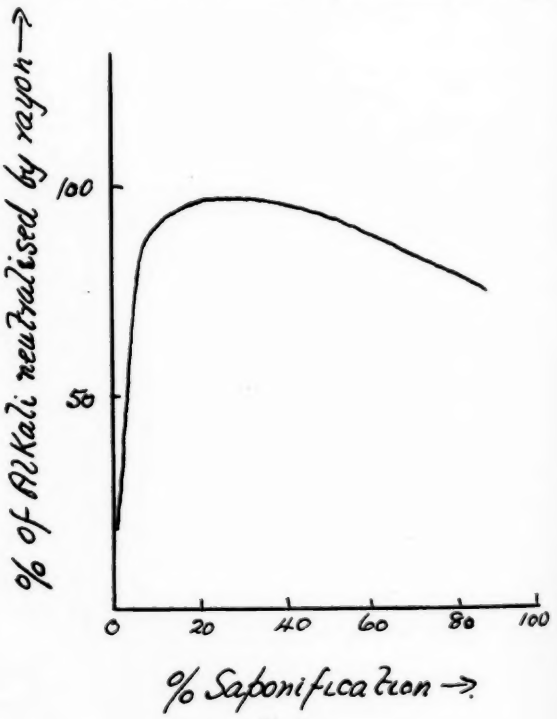



*Fig. 3*

are various methods. For instance in the case of a cotton-cellulose acetate fabric it is possible to saponify by treatment with a solution of a caustic alkali in a jig or by padding with a solution of an alkali and drying on ordinary drying cylinders. Again as the saponifying alkali

(Continued on page 607)

# Coloring Compound Fabrics Containing Cellulose Acetate

*By* **FRED. GROVE-PALMER, A.I.C.**

**The different methods of dyeing mixtures of fibres containing cellulose acetate rayon are taken up by the author in this article. It gives an outline of the saponification method which was formerly used in dyeing this class of fibre and it also gives the method of dyeing with the new colors. It includes mention of the dyestuffs which dye all fibres in one bath.**

CELANESE or, more properly, cellulose acetate rayon has forged ahead with remarkable rapidity; it has established for itself a position in popular estimation that is well-nigh unassailable on account of its beauty and many other qualities. The womenfolk of the world want it, they demand it, and they have to have it. But there is always another side to the shield; in this case it is the difficulty experienced by the dyer when the fabrics he is called upon to deal with are woven from mixed fibers. It is a question of getting the shade properly leveled without prolonged working which might lead to injury of one or other of the fibers of which the mixture is composed.

There have been several different methods of approaching the problem, all of which have been adopted, some more widely than others. One of these is to dye each yarn separately and then combine them on the loom. There are disadvantages here in that the shading up of each fiber takes much time and calls for close supervision; moreover, it may lead to the stocking of innumerable small lots of dyed yarns not in immediate demand, representing that much idle capital. Again, coloring instructions are not always given before the cloth is woven; it may easily be an order to get ahead with the weaving and await information as regards shades. It would be a fatal mistake to risk dyeing yarns in face of this. In any case, the method is of no use to commission dyers or any others to whom the fabric is given.

The other method has been to dye up the acetate yarn before weaving, and color the remainder of the cloth in the piece. Much the same fault is to be found with this plan as with the foregoing.

When it comes to dyeing fabrics that contain cellulose acetate, it has always been necessary to dye each fiber in a separate bath, carefully choosing such dyestuffs as will not be interfered with in the subsequent liquors and at the same time will not in any way stain or discolor either of the fibers they are not intended for. This can be done and is done often enough, but it is a tedious job even when the shades on the fibers are different; when there is a demand for perfect leveling it is not so easy and requires exceedingly close attention.

Fortunately, the latest developments in the dye-making industry have removed the difficulties almost entirely from the pathway of the much harassed dyer; he is now able to obtain dyestuffs which will go on to all fibers and will yield reasonably level shades on any mixture.

The call of modern fashion is mainly for mixed fabrics; the proportion of single fiber materials is growing rapidly smaller. Large numbers consist of two or three fibers, sometimes more, either as individual or mixed yarns. Obviously, when the dyer receives a cloth composed of silk, cotton, viscose rayon and acetate rayon, and sometimes a small quantity of woolen yarn, he has an equal number of chances of something slipping up in the dyehouse. Three or, perhaps, four different dyebaths each with its mixture of colors that must all together produce a perfectly uniform shade when finished, without staining or degrading each other, surely offers ample opportunity for liveliness all around. In addition to the technical difficulties, there are the practical ones of expenditure of time and labor while the cloth is progressing hither and thither through the dyehouse, occupying a series of dyeing becks and hydroextractors.

There is another aspect of the textile trade in which the appearance of cellulose acetate not infrequently gives rise to considerable trouble. This is in the redyeing of garments. It quite often happens that clothing sent for dyeing is fitted out with trimming of some kind made largely or entirely of cellulose acetate; the same with the linings of coats and opera cloaks. If these are thought to be only silk and cotton, for instance, and are treated as such, the appearance of the goods when the acetate comes up another color altogether can be better imagined than described. To speak truly, the position of these people is really worse than that of the dyer for in their case there is no chance of "putting it into black or some deep shade" by way of covering up a few mistakes.

Commission dyers, amongst others, who receive materials without a full and complete description, can be easily let down in a similar way. The shipment is received as, say, a silk and wool mixture. It is seen that there are certain effect threads or figures woven in, and the dyer might reasonably think that these were silk. Of course, it is easy to say that he ought not to think such things; he ought to test to make definitely certain, but even dyers are human. When the goods are dyed he has

an unpleasant awakening from his dreams of a pleasing profit if he has not quoted for the extra time and work involved in putting the whole batch through the acetate dyeing bath, to say nothing of the cost of the dyestuff required.

Of course, the solution of the whole difficulty was known from the beginning but its attainment was not then possible. This was the introduction of dyestuffs that would have the power of being absorbed by all fibers equally so that any mixed fabric should be no more trouble to handle in the dyehouse than one consisting of a single fiber. For many years this has been hoped for and now, at last, that hope has been realized.

There are now on the market two brands of dyestuffs suited to dyeing of materials containing any fiber—animal, vegetable, or artificial, including cellulose acetate. A great amount of research work has been carried on and the result has been that in each brand there is a range of eight colors at the moment of writing, but as work proceeds these will undoubtedly be added to until it will be possible to purchase any desired shade.

There will probably not be a single dyer throughout the length and breadth of the land who will not hail with acclamation this newly found possibility of dyeing uniformly leveled shades upon the hundreds of different classes of materials containing two, three, four or even more fibers. Truly it may be said to be a epoch marking advance in the technical history of the dyehouse; some one has even gone so far as to say that the year 1930 should be marked as the *anno mirabilis* of the textile industry. Before we had cellulose acetate, the processes involved in the dyeing of a cloth woven from animal, vegetable and artificial yarns was, comparatively speaking, not too difficult; it was necessary to employ two baths, of course, and each of these had to contain very carefully selected dyestuffs in solutions at exactly the right temperatures, and with the assistants best suited to the acid and substantive colors employed. Great care and attention to detail are required, there is no doubt, but, though it takes a moderately long time, the dyer of experience can safely gamble on getting the result desired by his customer. When the acetate came into fashion, with its very different reaction towards the normally used dyestuffs, it necessarily added still further complications, even when it was to appear in the finished goods in a contrasting shade. It was done; there is very little that the dyer will not do when he is put to it but it was hard work, and we shall probably never be able to estimate the value of the materials that have been spoiled in the endeavors to obtain colors suitably leveled up. All the old methods became so much junk when applied to cellulose acetate though they were useful enough for the other fibers.

One process of dyeing this form of rayon that seemed likely to find favor was the saponification method, which altered the chemical structure of the yarn by treatment with an alkali. Obviously, this was merely a make-shift, walking around rather than cutting through the problem. Cellulose acetate at its best is not a particularly strong material; this treatment still further weakened it and, at the same time, it detracted more than a little from its natural luster. This might not be looked upon as a fault at the present time but a few years since the principal charm in the eyes of the majority was the brilliancy and gloss of artificial fibers, then mistakenly though amusingly described as "silky." Although the reduction of luster would not now be regarded as a detriment, the weakening undoubtedly is, and in addition, the alkaline treatment also deteriorates the structure of both the woolen and silk yarns, if they happen to be constituents of the fabric. For these causes, the saponification process soon fell into disuse in most dyeworks, and research laboratories produced dyestuffs that had a real affinity for cellulose acetate in its normal condition. These are of excellent quality in every respect and do their work well, giving all the fastness to light, washing and milling that can be desired; at the same time, when used to color the acetate in mixed cloths, they add one more distinct process to the routine of dyeing, involving the entering and working in the dye liquor, washing, hydroextracting, and the necessary handling which must be incurred. All this not only adds considerably to the expense of the dyeing operations, and increases the length of time that the material is lying around in the dyehouse, but it also adds very largely to the risks of spoiling the material, either by accident or through prolonged treatment. Always the object is to cut down the handling to the minimum as regards time and operations concordantly with getting the desired results; obviously, then, this additional process is a disadvantage.

One is quite justified in saying that the newly introduced all-fiber dyestuffs, which will do the work in one bath, have very effectively bridged that gulf which lies between the dyer's work and his night's rest. Without going so far as to say that all his difficulties have been swept away, it may be stated that they have been considerably lightened to an extent even greater than they were before cellulose acetate made its appearance on the world's markets. It has yet to be seen to what degree the new range will be generally adopted but, though it would be unsafe to prophecy, there is not much doubt that the experimental instinct of the dyer will not allow him to pass up on this opportunity for improving his technique. The leveling of the shade in a monochrome poly-fiber fabric is no longer the pessimistic dream of the crepehanger; it can be done in one bath.

One make of these dyestuffs contains the following shades:

Yellow G
Red B
Brown G
Dark Green B
Light Green G
Saxe Blue R
Navy Blue B
Black DB

In all cases, swatches of mixed yarns: woolen, silk,

cotton and cellulose acetate evince excellent uniformity; the quantity of dyestuff used is quite normal, running between 1.5 and 4 per cent for light and medium shades, and up to 10 per cent for the Navy and 20 per cent for the Black. It would be possible, perhaps, for the ultra-critical to pick a quarrel over some of the fibers, but taken from a commercial standard of average high grade there is not much to grumble over.

The dyeing process is simple enough and the preparation of the liquor has no snags. It consists in pouring boiling water right on to the dye and stirring it continuously until the solution is complete. It is then poured through a muslin or fine wire gauze or strainer into the beck full of water in which has been dissolved from 10 to 40 per cent of Glauber's, according to the depth of the shade, as in ordinary work. A word of advice may not be out of place here; the makers of this class of coloring matter also recommend the alternative use of common salt as an assistant in the dye bath, but in all cases where there is the possibility of silk being present, this should be very carefully kept away from the dyehouse chemical bench. Sodium chloride is apt to give rise to spotting and tendering on silk fabrics, especially in warm weather or if stored in a warm warehouse.

As regards the best temperature for entering the goods, it has been found that a rather hotter bath than usual brings the best results; the liquor should therefore be warmed up to between 82 and 85 deg. C. and be maintained at that figure during the thirty minutes or so that working is continued. It may be necessary when dyeing dark colors to prolong the working for a further quarter of an hour, especially to get depth and fullness in the black.

When the shade is correct, the batch is lifted and washed well, first in hot and then cold waters, in the usual way; it is then ready to go forward for processing along normal lines. It will be noted that there is here no call for the use of developers to bring up the right color, nor for any other after-treatment.

The second brand of the all-fiber dyes contains an equal number of members but not, perhaps, in such a variety of shades; they are:

Yellow J
Orange R
Red J
Brown 5R
Saxe Blue 4B
Navy Blue R
Navy Blue 5R
Black S

Swatches containing a variety of fibers similar to that previously mentioned are equally well leveled in all colors. They can be treated with a uniform percentage of three for the first five shades mentioned above, and 8 per cent for the Navy Blues, with 15 per cent for the Black. These figures give good full tints in all cases with little if any differentiation between one fiber and another, though the duller yarns may appear slightly deeper than those having a higher luster.

The dyeing routine which is found to yield the best effects with this type of dyes, will be seen to vary slightly from that described for the former make; briefly stated, it is as follows:

The material should be previously well scoured in any normal wash liquor. The one named below has been found generally useful for this purpose:

| | |
|---|---|
| Marseilles soap | 4 lbs. |
| Ammonia | 1 gallon |
| Water, softened to zero hardness | 120 gallons |

The goods will need working for about thirty minutes in this at a temperature around, but not much above, 60 deg. C. A rinse in warm water follows and the batch is then whizzed moderately dry.

As before, the dyestuff is stirred in boiling water to effect complete solution, and is then poured through the sieve in the water which has been heated to the same temperature as the soaping bath. The goods are now entered without the addition of any assistant, and temperature is raised, fairly rapidly, to between 75 and 80 deg. C. It is kept at this while the material is being worked for a full half hour. It is not until this stage has been reached that the Glauber salt should be added, the quantity required lying between 20 and 30 lbs. for a bath containing 120 gallons. The temperature of the liquor is still kept at the higher figure mentioned, or a little beyond it, for thirty minutes more. It may not take quite so long as this, though, on the other hand, the darker shades may want a little longer. This, of course, is a matter for individual experience. A bath in which the proportion of liquor is around 2¼ gallons to one pound of cloth is found to give the most satisfactory conditions of working.

It sometimes happens that the bath is not fully exhausted in the specified time; if this occurs on several occasions, the additional time for working in the liquor should always be given after the addition of the Glaubers, not before. When there is a tendency for the color to go on to the silk and woolen fibers rather too quickly, the opposite effect may be obtained by the addition of a small quantity of soap solution to the bath. The amount required varies with the quantity of the animal fibers present, of course; suggested weights are from 2 to 4 lbs., dissolved in soft water of temperature equalling that of the bath. In the opposite case when it is required to hasten the absorption of the dye by the silk and wool, acetic acid may be added in quantities similar to those recommended for soap.

It does happen occasionally that the presence of very tightly twisted yarns causes them to appear a little less full in shade than the surrounding fibers. In such cases it may be necessary to top up in order to get the matching up satisfactory. For cotton and viscose, a small quantity of the appropriate mixture of substantive dyes is dissolved in the normal way and added to the bath in which the main dyeing has taken place. The shading

of the animal fibers will be done with an addition of suitable neutral dyeing acid colors, and for the cellulose acetate, a little of any of those dyestuffs specially intended for this form of rayon will bring up to the desired shade.

It should be specially mentioned that any of the colors in each range can be used together to produce other shades; this is a point which adds to the usefulness of the somewhat limited number at present placed on the market. As others become available the utility of the all-fiber colors will be greatly increased.

The after-dyeing processes follow the normal lines; they are the rinsing and finishing. The usual scrooping bath may be used, though there would appear to be a tendency during recent months to omit this, and for rather an interesting reason. The scroop is put into fabrics, as is well known, in order to give them a crispness and crunchiness, spoken of twenty-five years ago as *frou-frou;* the sound of this "swishing" was at least a sign of wealth if of nothing else. But now comes in a modern scientific invention which has made that once-pleasing sound unpleasant. The invention in question is the talking film; for purposes of reproduction of sound in the cinema studio there may be no extraneous noises and it was necessary to put a stop to the rustle of the actresses' clothing, if any. Consequently, cloths were prepared without the added scroop, and as the fashion influence of the film star is very considerable, in all parts of the world, the custom of wearing noiseless dresses is gradually spreading up into all other grades of society.

As regards the action of the new dyes, we recall that it has been the considered opinion of workers on the subject, that the final success of a color bath is a factor of the fine state of division of the dyestuff when in use: in other words, the better the dispersion the better the dyeing. It stands to reason that the fibers can take up more color and absorb it more deeply if it is fine rather than coarsely broken up. In the case of the animal fibers, wool and silk, this absorption of the dye is caused by certain chemical reactions which take place between acid and basic groups present at the time of dyeing. Consequently, the quantity of finely divided acid dye that can be absorbed by the proteid substances in those animal fibers is a measure of the quantity of basic groups the fibers contain. The basic compounds present have been isolated as the result of research, and have been designated: histidine, lysine and arginine.[1] Recent work in dyeing leaves no doubt that better and more even results can be obtained when the whole matter is subjected to the control of the hydrogen-ion concentration of the liquors. In a manner somewhat similar to that of silk, the dyeing of cellulose acetate depends upon the equilibrium between bases and acids, and it is with a view to producing the balanced effect that the special celanese dyes have been built up.

The introduction of these all-fiber dyestuffs will undoubtedly bring about a new outlook towards cellulose acetate rayon. In a recently published book, this fiber is alluded to in the following terms:

> "On the whole, acetate silk (sic) is an extremely interesting material, one of its particular advantages being the use which can be made of it in the production of mixed fabrics. If, for example, fabrics of viscose silk and acetate silk, real silk and acetate silk, or viscose, real silk and acetate silk are to be dyed, it is possible by using suitable dyes without any other treatment to leave the acetate silk perfectly white. It is also possible to dye the acetate silk on its own account at the same time, so that very pleasing two and three-color effects may be obtained."[2]

Apart from the constant misuse of the word "silk," that paragraph may be regarded as being remarkable in that it seems to make a virtue of necessity, turning to account the lack of affinity of cellulose acetate for the majority of dyes. This is all to the good, but now there is no longer the need for it. With the introduction of these "all-purpose" dyestuffs, the fabric dyer can see, if not altogether the end of his troubles, at least a very great advance along the road that leads to that ideal simplicity of treatment that we have been looking forward to for so many years.

[1] Chapman, Greenberg & Schmidt, J. Biol. Chem., 1927, 72, p. 797.
[2] Schober, J., "Silk and the Silk Industry," London, 1930.

## 1931 Year Book

The 1931 edition of the National Association of Cotton Manufacturers Year Book now being distributed to mill executives in the cotton manufacturing countries of the world maintains the standards of excellence which has made the publication the most comprehensive reference work on the cotton industry in existence.

The compilation of data of interest to the manufacturer has been effected with the utmost care and is more thorough than ever before. Government authorities in this country and abroad have cooperated in supplying much of the data. The present volume which is the 14th of the series has been prepared with the end in view of presenting all of the information which manufacturers and other interested persons might want relative to the industry.

Annually since the printing of the first Year Book in 1918, changes have constantly been made and suggestions as to how the book could be made more valuable have been considered and acted upon. The book is divided into two main sections, the Statistical and the Technical.

Because of the present situation with regard to supplies of the raw material on hand the review of the last eight American cotton crops, given in concise fashion in the fore part of the volume, is of particular interest.

The statistical section has been brought up to date and in addition to many new tables the statistics also include more subdivisions by classes of fabrics and divide the production of cloth into groups of fabrics with yarn numbers averaging 40s and below and above 40s.

# The Weighting of Silk

*By* **WALTER M. SCOTT, Ph.D.**

*Consulting Chemist with Gustavus J. Esselen, 73 Newberry St., Boston, Mass.*

## CHAPTER III. CHEMICAL ANALYSIS AND CONTROL—RAW MATERIALS.

**This is the third in a series of articles on the weighting of silk. The first two have appeared in the two previous issues of the AMERICAN DYESTUFF REPORTER. The first chapter incorporated and historical study of the subject and the second chapter described in detail the present day methods of weighting silk. This installment considers chemical analysis and control and the one appearing in next issue will compare the relative durability of weighted and unweighted silk.**

### TIN SALTS

1. Pink Salt, $SnCl_4 + 2NH_4Cl$. As indicated by the formula this is a double salt of stannic chloride and ammonium chloride. It was one of the first tin salts to be recommended for the weighting of silk and was formerly used in large quantities, but it has now been almost entirely replaced by straight stannic chloride.

Pink salt is a crystalline product and hence is not subject to many impurities. The chemical analysis is usually confined to a determination of tin by the method described under stannic chloride. According to the formula the theoretical percentage of tin is 35.8% and the commercial product should run pretty close to this figure. It should be practically free from iron so that not more than a faint coloration is obtained in the qualitative test with potassium ferrocyanide or ammonium thiocyanate.

2. Tin Crystals, $SnCl_2 . 2H_2O$. Stannous chloride is at the present time practically always sold in the crystalline form under the commercial name of Tin Crystals. Although not as widely used as stannic chloride for the weighting of silk, it is nevertheless quite well known in the silk industry. It is chiefly used in connection with logwood, catechu, gambier or similar extracts as one of the sources of weight for black dyed silks.

*Determination of Tin Strength*

Weigh 0.6 to 0.8 grams of tin crystals into a beaker and dissolve in 50 cc. of dilute hydrochloric acid. To the solution add slowly, with stirring, a 10% solution of ferric chloride until there is an excess present (as shown by the yellow color). Then dilute and titrate with N/10 potassium permanganate. Calculate as Sn. The average analysis of commercial tin crystals should be 51.5% tin. In a qualitative test for sulphates by adding barium chloride to a solution of tin crystals acidified with hydrochloric acid, there should be no turbidity, or at the most, only a very faint trace.

3. Tetrachloride of Tin, $SnCl_4$. In the early days stannic chloride was sold either in the crystalline form (sometimes called "Butter of Tin") combined with five molecules of water, or in aqueous solutions of a definite specific gravity. Of late years the manufacture of anhydrous stannic chloride has been perfected and at the present time by far the largest proportion is sold in this form. The anhydrous product is a clear colorless liquid of 2.26 specific gravity and contains 45.4 per cent of tin. When exposed to the air it gives off copious white fumes which are rather obnoxious to breathe and therefore the customary practice is to convey it by means of a syphon directly from the drum into a tank of water in order to form a stock solution. A stock solution of convenient strength is formed by syphoning the contents of two drums of anhydrous tetrachloride of tin into about 160 gallons of water, then adding two carboys of muriatic acid (20° Bé.) in order to prevent any hydrolysis of the tin salt and keep the solution clear.

Whether the stannic chloride is purchased in the crystalline or anhydrous form it is more convenient to convert it into a stock solution before taking a sample for analysis. The following factors are determined:

*Specific Gravity*

Determine with the hydrometer at room temperature.

*Tin*

Pipette out 1.5 cc. of the solution, add 75 cc. of boiling water and leave on the steam bath for 30 minutes. Then decant into a filter or gooch crucible six times, finally washing with hot water until entirely free from chlorine. Test the washings for chlorine with silver nitrate. Dry the precipitate, ignite and weigh as $SnO_2$. Calculate as Sn.

*Total Acidity*

The filtrate from above, containing all the hydrochloric acid, is titrated with decinormal alkali using methyl red as an indicator. Calculate as HCl.

*Free Acid*

The theoretical amount of hydrochloric acid which would combine with tin to form $SnCl_4$ is calculated and then subtracted from the total acidity found by titration. The remainder represents the free acid.

A typical stock solution of stannic chloride having a specific gravity of 56.5° Bé. should contain approximately 25.0% of tin and 1.5% free acid as HCl.

4. Sodium stannate, $Na_2SnO_3$. This salt has at various times been recommended for the weighting of silk but is practically never used at the present time. Because stannic acid is a very weak acid the sodium salt gives a distinctly alkaline solution and is more detrimental to the silk fibers than the acid tin salts. It is relatively so unimportant for weighting purposes that it does not seem necessary to describe methods for its analysis.

### Disodium Phosphate, $Na_2HPO_4 \cdot 12H_2O$

This is very often spoken of as the normal sodium phosphate to distinguish it from the acid monosodium phosphate and the more basic trisodium phosphate. It is usually sold commercially under the name of "Phosphate of Soda." As indicated by the formula it crystallizes with twelve molecules of water and is practically always sold in this form.

#### *Quantitative Estimation of Phosphate*

Weigh out 2 grams of the sample and dissolve in 100 cc. of water, then add 20 cc. of 10% ammonium chloride solution and slowly pour in the magnesium mixture with constant stirring, 10 cc. of this mixture for every 0.5 gram of sample used. (Note: The magnesium mixture is prepared by dissolving 55 gm. $MgCl_2 \cdot 6H_2O$ and 70 gm. $NH_4Cl$ in 350 cc. $NH_4OH$, concentrated, and diluting to exactly one liter with distilled water.) Finally add 40 cc. of concentrated ammonium hydroxide slowly, continuing the stirring. Let stand over night and filter on a gooch, washing with water containing one-third its volume of dilute ammonium hydroxide. Ignite and weigh as $Mg_2P_2O_7$. Calculate as $P_2O_5$.

#### *Alkalinity*

Determine the pH of a 1% solution of the sample colorimetrically, using thymol blue as the indicator.

#### *Qualitative Tests*

Test for the presence of sulfates with a solution of barium chloride, and for the presence of chlorides with a solution of silver nitrate. If either of these are present in noticeable amounts, they may be determined quantitatively.

A good commercial grade of disodium phosphate should yield approximately 20% of phosphoric anhydride in the analysis as described above. In a 1% solution it should show a pH of approximately 9.0, in contrast to monosodium phosphate which has a pH of about 3.5 in 1% concentration and trisodium phosphate which has a pH of about 11.0 at a concentration of 0.1%. It should not contain more than a trace of sulfates or chlorides.

### Sodium Silicate

This is normally sold to the textile trade in the form of a syrupy solution under the names of "Silicate of Soda" or "Water Glass." There are a number of brands which differ in the relative amounts of silica ($SiO_2$) and soda ($Na_2O$) and in the proportion of water. For silk weighting purposes the ratio of $Na_2O$ to $SiO_2$ is preferably about one to three.

#### *Specific Gravity*

Determine with the hydrometer at a temperature of about 20° C.

#### *Sodium Oxide*

Weigh out ½ to 2 grams of the liquid in a covered vessel such as a porcelain crucible covered with a watch glass. The sample is dissolved in about 80 to 100 cc. of water, heating if necessary, then titrated with fifth normal hydrochloric acid using methyl orange as an indicator. The results are calculated as $Na_2O$.

#### *Silica*

To the solution from above add an excess of hydrochloric acid. Evaporate down to dryness three times without filtration between, moistening the residue with concentrated hydrochloric acid after each evaporation and before any water is added. The resulting residue of silica is filtered off, ignited and weighed as $SiO_2$.

The ratio of sodium oxide to silica is determined by dividing the percentage of $SiO_2$ by the percentage of $Na_2O$. The type of silicate solution, which is usually furnished to the silk trade, has a specific gravity of approximately 42° Bé. and contains about 10% $Na_2O$ and 30% $SiO_2$.

### Hydrochloric Acid (Commercially Called Muriatic Acid)

#### *Specific Gravity*

Determine with the hydrometer at a temperature of about 20° C.

#### *Acidity*

Weigh into a glass stoppered weighing bottle 0.2 to 0.4 grams of the sample. Wash into a beaker and dilute with distilled water, then titrate with N/10 NaOH using congo red as an indicator. Calculate as HCl.

#### *Residue*

Pipette 100 cc. of the sample into a weighed evaporating dish. Evaporate to dryness on the steam bath then heat for at least one hour in the oven at 100° C. Cool in a desiccator and weigh.

Average Analysis of Commercial Muriatic Acid

| | |
|---|---|
| Specific Gravity | 1.16 |
| Acidity as HCl | 30.0% |
| Residue | not over 0.2% |

### Standing Baths

In carrying out the standard process for the weighting of silk with tin salts as described previously in this article, there are three baths which require a certain amount of supervision and chemical control, namely, the tin bath, the phosphate bath and the silicate bath.

### The Tin Bath

Different operatives have different preferences with respect to the strength of the standing bath containing stannic chloride, also with respect to the amount of free hydrochloric acid in this bath. In general, with a smaller percentage of free acid the tin is absorbed by the silk faster but not as uniformly while an increase in the percentage of free acid retards the speed of absorption but increases the uniformity. In any case there must be sufficient free acid so that there is no precipitation of stannic hydroxide in the bath during the weighting process, and the maximum limit is set by most operators at 1.5% HCl. Experiments have shown that the best compromise between

speed and uniformity of absorption is found with 0.5% free hydrochloric acid.

The standing tin baths are tested for specific gravity, tin strength and free acid in the same manner as described previously for the stock solution of this chemical. Below are listed the analyses for typical examples of a strong and a weak tin bath:

| | Specific Gravity | Tin | Free HCl. |
|---|---|---|---|
| Strong tin bath | 30.2° Bé. | 12.8% | 0.5% |
| Weak tin bath | 22.4° Bé. | 9.3% | 0.5% |

The strength of either bath is brought up to the correct point by adding the required amount of the stronger stock tin solution. If the percentage of free acid is below the mark it is increased by the addition of a calculated quantity of muriatic acid. On the other hand, if the percentage of free acid is high it is reduced by the regulated addition of ammonia.

### The Phosphate Bath

The strength of the phosphate bath is usually determined by its specific gravity. There is more agreement between different operatives with regard to the phosphate than with regard to the tin bath. In fact the phosphate solution is practically always maintained at such a concentration that the gravity will register from 4 to 6° Bé. If the gravity has been reduced below 4° Bé. the solution may be strengthened by dissolving an additional quantity of solid sodium phosphate directly in the standing bath or by adding the requisite amount of a stronger stock solution of sodium phosphate. The latter procedure is always used in connection with the continuous weighting of piece goods as described earlier in this article. Here the phosphate solution traverses the machine in the opposite direction to the passage of the goods and gradually gives up its strength. After it emerges from one end of the machine it is passed back to the opposite end again and at some convenient point on the way it is brought back to its original strength by an addition of the stronger stock solution.

Supplementing the specific gravity determination the standing baths may be analyzed for phosphate strength and for alkalinity as described previously for sodium phosphate under the heading of raw materials. However, if the gravity is carefully watched or automatically controlled it is only necessary to make these additional tests once in a while as an extra check. Below are listed the strengths of typical phosphate solutions:

| Specific Gravity | $Na_2HPO_4$ | $P_2O_5$ |
|---|---|---|
| 4.0° Bé. | 3.2% | 1.7% |
| 5.0° Bé. | 3.8% | 2.0% |
| 6.0° Bé. | 4.4% | 2.3% |

If the wash after the tin treatment has been carried out with sufficient thoroughness it is rarely necessary to correct the alkalinity of the phosphate bath. However, in some cases a little of the acid may be carried over from the tin bath and thus reduce the alkalinity of the phosphate bath. Whenever this happens the proper alkalinity must be restored by the addition of a little ammonia.

### The Silicate Bath

The strength of the silicate bath is practically always measured in terms of its specific gravity. Inasmuch as the concentration of this bath is a direct factor in determining the amount of weighting which is transmitted to the silk it is usually varied somewhat according to the needs or the preferences of each individual operative. In general, however, the specific gravity of the silicate bath is kept between 3 and 5° Bé. When the concentration is reduced below the required point the solution is strengthened by the addition of fresh silicate in the form of the raw material as purchased, or of a stock solution as in the case of the sodium phosphate.

It is possible to analyze the standing bath of silicate in the same manner as previously described for the raw material but it is seldom necessary to do this. As long as the uniformity of the shipments of silicate is maintained, the specific gravity is a sufficient check on the strength of the standing bath.

### Analysis of Weighted Silks

There have been proposed a number of methods for the quantitative analysis of weighted silk. Most of these methods are based on the principle of using some solvent which will dissolve out the weighting material and leave the silk behind. A standard procedure of this type has been recommended by the United States Bureau of Standards and their directions for carrying out the analysis are reprinted below with the permission of the Bureau.

"In order to have a representative sample, it is preferable to use a strip of cloth taken from selvage to selvage and weighing from 3 to 5 grams. Spread the sample loosely on a watch glass and dry for 1½ hours at 105 to 110° C. Transfer to a tared weighing bottle, cool in dessicator and weigh. The weight of the sample is designated weight A. The analysis is based on the weight of the dried sample."

### "Finishing Materials"

"Digest the sample in 90 to 100 times its weight of distilled water at 65 ± 1° C. for 20 minutes with occasional agitation. Decant the liquid and squeeze by hand. Rinse the sample by placing it in 40 to 50 times its weight of distilled water and heat with agitation to 65° C. Decant the rinse liquor and repeat the rinsing treatment twice more. Squeeze the sample by hand and rinse with two 30 cc. portions of warm alcohol, agitating it in each for about 2 minutes. Treat similarly with 2 portions of diethyl ether at room temperature, squeeze and air dry for about 10 minutes.

"Drop the sample into a beaker of boiling water and let stand for 5 minutes, remove, squeeze, spread out on watch glass and dry for 1½ hours at 105° to 110° C. Place in tared weighing bottle, cool in dessicator, and weigh. This weight of the sample is called Weight B. The material removed in this treatment is taken to be 'finishing materials.' The amount of 'finishing materials' in per cent is $\frac{A - B}{A} \times 100$."

"Total Weighting"

"The sample from which 'finishing materials' have been removed is placed with 90 to 100 times its weight of hydrofluoric-hydrochloric acid reagent ((see *a* below) in an 800 cc. tall-form Pyrex beaker, and heated uniformly to 55 ± 1° C. It is kept at this temperature for 20 minutes, agitating occasionally. The acid liquor is then poured off and the sample is treated with about 200 cc. distilled water at 55° C. for about 5 minutes with stirring. This treatment is then repeated with a fresh portion of distilled water, and the sample is removed and squeezed by hand."

The treatment outlined above, beginning with the addition of the acid reagent, is repeated. Then a similar treatment is given but using sodium carbonate (see *b* below) solution in place of the acid reagent. Then the acid treatment is repeated twice more, after which the sample is treated with alcohol, ether and boiling water as described in the procedure for the determination of "finishing materials." The sample is dried and weighed as previously described and this weight is called C. It represents the weight of silk fibroin and residual ash.

The ash is determined by igniting the sample after the above extraction process. Although the amount obtained as ash is generally negligible, the determination should be made when accurate results are required and as a check on the previous treatments. The treated sample is put in a tared crucible, and placed in an electric muffle furnace at about room temperature. The temperature of the furnace is regulated so that in 2 to 2½ hours, the furnace reaches a temperature of 750 to 800° C., and is held there for ½ hour. The combustion chamber should have a vent in the rear and near the top and the door should be raised about 4 millimeters at the front; this permits the free escape of gases and the admission of a gentle current of air by convection to effect complete combustion of the carbonaceous materials. The weight of the ash is called weight D.

The "total weighting" on the silk is taken to be all substances that are not silk fibroin. The amount of "total weighing" in per cent is:

$$\frac{A - C - D}{A} \times 100$$

The reagents called for above are:

a. Hydrofluoric-hydrochloric acid reagent; Contains two per cent by weight of hydrofluoric acid and two per cent by weight of hydrochloric acid in distilled water.

b. Sodium carbonate solution; Contains two per cent by weight of anhydrous sodium carbonate in distilled water."

Addenda to Chapter I

In Chapter I of this article on Page 518 it is stated that the first mention of tin in combination with sodium phosphate and sodum silicate was made in the year of 1897. The author has subsequently been informed that although the first United States patent was not issued until 1897, the actual process was in use in this country at the plant of the Weidmann Silk Dyeing Company as early as 1892. Acknowledgement for this information is made to Mr. Carl Bengs who was one of the pioneers in the tin weighting of silk.

# Pan-American Commerical Program Contacts Dyestuffs

*By* Waldon Fawcett

WHATEVER of the future destiny of the American dyestuffs industry lies in export trade is due to be influenced by a Conference to be held at Washington, D. C., from October 5 to 12. This is the fourth in a series of Pan-American Commercial Conferences held over a period of years. Held under the auspices of the Pan-American Union, the object is to bring together commercial leaders from twenty-one American republics to the end that all the processes of international trade interchange may be smoothed and standardized.

Prediction that the present undertaking will overshadow all previous efforts to facilitate commerce between the three Americas is not implausible. For one thing, this meeting of the league of Western nations assembles in the midst of a business depression which has borne particularly heavily upon many of the nations of Central and South America and the West Indies. Even more to the point, is the circumstance that this gathering is specifically dedicated to the cause of the removal of the trade barriers which hamper inter-American trade.

The fundamental purpose of the various successive Pan-American Commercial Conferences has been to consider all obstacles, direct and indirect, that tend to hinder commerce. The autumn of 1931 finds the problem clarified if not simplified by the fact that, in this tense economic era the obstacles to the free and rapid flow of trade stand clearly revealed. Customs tariffs and other restrictions on import and export trade will be dealt with from an unusual angle. In the majority of the international conferences of the past few years at which customs tariffs have been considered, the discussion has been predicated on the situation that exists in Europe. Here the parties to any arrangement are countries which are largely industrial and which seek to fix tariff rates at a level designed to keep out foreign manufactures and reserve the home markets for domestic manufacture. At Washington, the issue is to be approached from the standpoint of the countries of the American Continent in most of which tariffs are levied primarily for revenue purposes and not to exclude foreign products.

Interlocking with the discussion of trade barriers will be the consideration by the Conference of possibilities for the development of inter-American commercial relations by means of general or special economic agreements. This is a subject which suggests extensive possibilities in encouragement of the U. S. color industries. Because, the agreements of special character which are to be considered as mediums of closer trade relations are of the type of the existing agreement between the United States and Cuba which provides for a preferential rate on certain commodities entering the trade between the two nations.

(Continued on page 607)

# Chemical and Physical Properties of Carbon Tetrachloride, Its Advantages As A Commercial Cleaning Fluid*

*By* **PAUL S. BRALLIER**
*Technical Director, Niagara Smelting Corp.*

**This article compares carbon tetrachloride with other solvents used in dry cleaning. The following phases of the subject are discussed: Solvent action, volatility, flammability, odor, corrosion of metals, purification of solvent, distillation and health hazard.**

CARBON Tetrachloride is a rather formidable name for a very interesting and valuable solvent. As a matter of fact, if the name is examined closely and without too much respect for its technical sound, it will be found to be a straightforward family name. The solvent is composed of the two elements, carbon and chlorine; and the prefix "tetra" means only that there are four atoms of chlorine present for each atom of carbon.

CARBON TETRACHLORIDE

*A Simple, Synthetic Chemical Compound*

(A)—Carbon

(B)—Chlorine

Unlike many familiar liquids, Carbon Tetrachloride is a strictly synthetic compound. It exists as a result of some chemist's curiosity as to what would happen if chlorine and carbon were caused to combine. The fact that it is a simple chemical compound gives it very definite and characteristic properties and further makes possible its manufacture with a uniform high standard of purity.

COMPARISON OF DRY CLEANING SOLVENTS

The properties of carbon tetrachloride are such as to make it desirable for use in dry cleaning. The purpose of the present discussion is to compare carbon tetrachloride with gasoline, naphtha or Stoddard solvent for dry cleaning purposes, and it might be well as a beginning to outline what would be desirable in an ideal dry cleaning solvent and then see how they measure up. In speaking of Stoddard solvent, the intention is to include all of the so-called "safety" naphtha solvents which have the same general specifications as does Stoddard solvent.

An ideal solvent should remove all dirt and stains but should not have an injurious effect on fabrics or dyes. An ideal solvent for dry cleaning ought to take out all the dirt and stains and have no effect on fabrics and dyes.

*The Ideal Solvent Should Be*:

(a) Volatile—for quick drying.

(b) Without odor.

(c) Capable of recovery—to reduce cost.

It ought to be volatile enough so that fabrics cleaned in it will "dry" readily.

*It Should Not Be*:

(a) Inflammable or explosive.

(b) Corrosive to equipment in which it is used.

It ought not to be flammable or explosive. It ought to be without odor, or at least without an unpleasant odor.

It ought not to affect adversely the equipment in which it is used. To be effective and economical it should be capable of ready purification and recovery for re-use, so that the work being done can always be treated with clean solvent without excessive solvent cost.

CARBON TETRACHLORIDE

(a) Removes dirt, oil and greases.

(b) Leaves no odor.

(c) Is volatile.

(d) Is not inflammable or explosive.

(e) Is readily purified and recovered

Obviously the most important feature of any solvent is its ability to remove dirt and stains without affecting fabrics or dyes. If you had only one kind of dirt and stain and only one kind of fabric and dye, there might be some chance of finding a solvent which would fully meet this requirement. Since, however, many different kinds of substances may be involved in dirt and stains and may occur on many different fabrics in connection with all classes of dyes, it must be realized that a "perfect" solvent in this respect is more likely to be hoped for than attained. The best solvent will be the one that comes nearest having this desired selective action.

In connection with the cleaning action of these solvents, a study of the used solvent from a commercial dry cleaning plant has been made and has been found interesting. Such studies may be readily carried out with carbon tetrachloride because it can easily be separated from the impurities which it takes out.

A sample was taken from a batch of carbon tetrachloride which had been employed in a commercial establishment for general dry cleaning. This was found to contain 2.48% of "dirt" and 97.52% of carbon tetrachloride. The "dirt" was found to be made up of two

*Paper presented before the Pacific Northwest Dyers and Cleaners' Association, Vancouver, B. C., Canada, Aug. 8, 1931.

general classes, one of which was soluble in carbon tetrachloride and the other insoluble. The soluble portion made up 28.46% of the weight of the dirt and the insoluble 71.54%. The soluble portion was a greasy semi-solid material of about the consistency of vaseline.

The insoluble portion was found to consist of 83.23% combustible and 16.77% non-combustible or mineral matter. The mineral matter contained oxides of silicon, iron, aluminum, calcium and magnesium, and from its composition might easily be regarded as a mineral dust such as might be expected to be present in the air. The analysis can be summarized as follows:

1—The used solvent contained—97.52% carbon tetrachloride. 2.48% "dirt."

2—The "dirt" consisted of:

(a) Grease and oil soluble in carbon tet.... 28.46
(b) Insoluble in carbon tet but combustible. 59.54
(c) Insoluble in carbon tetrachloride but non-combustible (mineral) ..... 12.00

From this, it would appear that in cleaning, the carbon tetrachloride has actually dissolved only about one-fourth of the "dirt" removed. The remaining three-fourths of the "dirt" consisted of solid material, which was evidently cemented to the fabric by the oil and grease. Of this solid material, more than 80% was combustible, and probably consisted of lint, short textile fibers, and other solids which might be said to be of organic origin. The remaining solid matter was non-combustible and evidently mineral in character, and had a composition that might be expected in road dust.

It is believed that this analysis throws a considerable amount of light on the mechanism of dry cleaning. The primary action of the solvent is to dissolve the film of oil and grease which is bound to accumulate on fabrics because of atmospheric pollution. The solution of this greasy film releases solid particles of foreign material which have been more or less cemented to the fabric by the film, and in this release the solvent effects its secondary cleansing action. These things being true, it is obvious that the solvent which will attack the grease film most readily and which has the minimum of "oily" qualities in itself, will perform the job of dry cleaning most effectively, provided its solvent activity does not lead it to attack the fabrics, or dyes on the fabrics, being cleaned.

Both carbon tetrachloride and Stoddard solvent will take out most of the dirt that dry cleaning is supposed to remove. However, a careful comparison of the two solvents in action will convince the observer that carbon tetrachloride is a more ready and a more active solvent than Stoddard solvent. If a piece of soiled fabric is divided and one part is cleaned in Carbon Tetrachloride and the other part in Stoddard solvent, it will usually be found that carbon tetrachloride has dissolved out a greater portion of the foreign material. This is not to say that it will take out all dirt and all stains. The fact, however, that carbon tetrachloride has long been used as a "spotting" fluid in connection with dry cleaning done with naphtha solvents indicates very clearly that it has a wider solvent range than do the naphthas.

### Stoddard or Safety Solvents

(a) Are explosive at a temperature of above 105°-110° F.
(b) Are combustible.
(c) Leave odor if not handled properly.
(d) Are not highly volatile.
(e) Are oily.

Further than this, Stoddard solvent is closely related to the mineral oils, and has some small degree of "oiliness" which is absent from carbon tetrachloride. The difference in the two liquids in this respect is quite evident to anyone who will take the trouble to rub the tip of his thumb and forefinger together in each liquid. The "oily" quality of Stoddard solvent, even though not great when compared to regular lubricating oils, is still sufficient to interfere in some degree with the secondary cleansing action of the solvent by removing the binder. Carbon tetrachloride, being without this oily quality, can be expected to give a greater degree of secondary cleansing.

### Volatility

The second item on our list of specifications for an ideal solvent is the degree of volatility. Carbon tetrachloride is much more volatile than Stoddard solvent. If an equal number of drops of carbon tetrachloride and Stoddard solvent are allowed to spread out on a piece of clean blotting paper, it will be found that the "wet spot" caused by Stoddard solvent requires from 20 to 30 times as long to disappear as does the spot from carbon tetrachloride. This indicates that fabrics cleaned in carbon tetrachloride will "dry" much more quickly than if cleaned in Stoddard solvent.

### Flammability

Carbon tetrachloride has a great and indisputable advantage over Stoddard solvent in that it is absolutely non-flammable, non-combustible and non-explosive, whereas Stoddard solvent only reduces the fire hazard. Carbon tetrachloride is not only free of any fire hazard but is actually used as a fire extinguishing agent since it is the principal constituent of extinguisher fluids such as Pyrene. Stoddard solvent, on the other hand, is "safe" only to the extent that it has been so prepared and refined that an exposed flame passed over the surface of the solvent will not ignite the solvent vapors until the liquid has been heated to a temperature of about 105° F. It is, however, distinctly combustible and its vapors become explosive once the liquid temperature exceeds 105° F. If a spark from any cause should occur in the tumbler while the solvent is being vaporized out of the load, an explosion might result. If a fire starts in an establishment using Stoddard or any petroleum solvent any solvent in the path of the flames is simply so much added fuel. Carbon tetrachloride under similar conditions would tend to extinguish the flames as soon as liberated.

### Odor

Whether or not an odor is pleasant is, to a great extent, a matter of personal opinion. Carbon tetrachloride is

usually described as having a pleasant, ethereal, clean odor (although some people claim to find the odor unpleasant). On the contrary, Stoddard solvent has the other characteristic of petroleum naphthas, and while its odor may not be especially objectionable if the solvent is kept pure and sweet, it is believed that very few people will be found who really like to have the odor of this dry cleaning solvent on their clothes.

Regardless of the question of the odor of the solvents themselves, carbon tetrachloride has a very distinct advantage in evaporating readily from the fabrics and leaving them at once entirely without solvent odor, Stoddard solvent, due to its less volatile nature, requires more heat and a longer drying and deodorizing period to rid the garments of odors, and it does not require an unusually sensitive nose to detect a solvent odor in clothes cleaned with Stoddard or similar solvents, especially if the solvent has not been kept in prime condition. The superiority of carbon tetrachloride in this respect is due to its greater volatility, which allows it to vaporize much more readily than Stoddard solvent, and also to the fact that carbon tetrachloride is a single chemical compound with a distinct boiling point, whereas Stoddard solvent is made up of a mixture of many related chemical individuals which have varying boiling points and rates of vaporization. The lower boiling or more volatile constituents of Stoddard solvent vaporize first and leave behind them the higher boiling or less volatile constituents. These less volatile compounds evaporate more and more slowly as the progressive evaporation continues and it is a matter of time before the final traces of solvent are removed.

### Corrosion of Metals

Carbon tetrachloride must be admitted to have a greater corrosive action on iron and steel than does Stoddard solvent. The action on steel, however, is comparatively slight so long as water is not present as a layer on top of the carbon tetrachloride, and manufacturers of carbon tetrachloride find it entirely practical to ship large lots of it in ordinary steel tank cars. Carbon tetrachloride is able to dissolve about 0.008 per cent of its own weight of water at ordinary temperatures. This small amount of moisture is not sufficient to make it seriously corrosive. If more than this amount of water is present, however, steel and some other common metals will be slowly attacked at ordinary temperatures, and more rapidly at temperatures approaching 170° F. These facts do not prevent the general use of carbon tetrachloride, however, because special metals and alloys are known which resist the action of carbon tetrachloride in the presence of water; and it is entirely practical to use these special metals where the presence of water is to be provided for.

Statements have been published to the effect that in the presence of water, carbon tetrachloride is decomposed with the formation of hydrochloric acid. This is true in a restricted sense and under certain special conditions. It has been demonstrated, experimentally, that carbon tetrachloride with a layer of water on top of it can be stored for more than a month at ordinary room temperatures in contact with these resistant metals *without the formation of even a trace of acid.* Carbon tetrachloride has been allowed to boil continuously for a week at a time in the presence of a layer of distilled water in glass apparatus and no evidence of acidity in the solvent was found at the end of the test. When the same continuous test was run with a resistant metal only 0.0067 per cent of the carbon tetrachloride had broken down to form hydrochloric acid, and similar test on mild steel indicated that 1.2 per cent of the carbon tetrachloride had formed hydrochloric acid. This boiling in the presence of a susceptible metal and in contact with a water layer is the most severe condition that is likely to be found in practice, and even here the rate of decomposition of the solvent to form hydrochloric acid is only a little more than 1 per cent per week for steel. It is less than one hundredth of 1 per cent for a resistant metal. Experience in commercial scale cleaning with tetrachloride has shown that there is no tendency for acidity to develop or build up in the solvent if proper metals are used. It should be obvious, therefore, that while there are conditions under which carbontetrachloride will break down to form hydrochloric acid, the reaction even under these most favorable circumstances is very slow. The mere contact of water and carbon tetrachloride does not lead to acid formation unless there are susceptible metals or other materials of like action present to promote the decomposition.

### Purification of Solvent

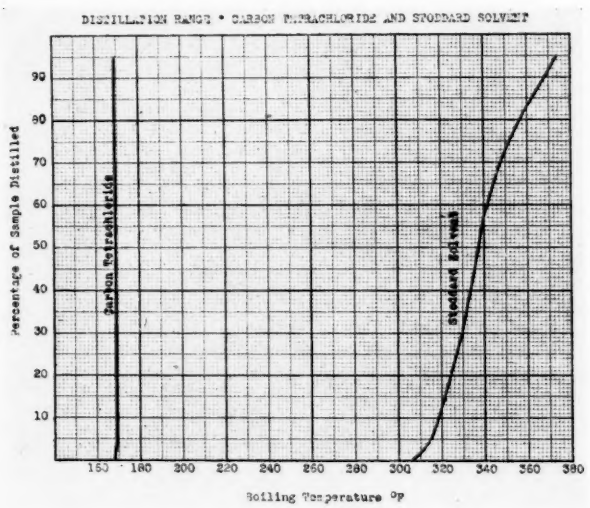
One of the most essential steps in the use of any dry cleaning solvent is the purification of solvent which has been used for cleaning so that it may be used again for further cleaning. There are two general processes for accomplishing this purification; first, chemical treatment in conjunction with filtration; and, second, distillation. Of these two, the distillation method gives the most effective and most nearly complete purification. The chemical treatment is somewhat complicated and even when augmented by filtration with dechlorizing agents, will not remove mineral oils or greases which may be taken up by the solvent. Chemical purification has been generally used with solvents of the Stoddard type because distillation of such solvents is not easy and the chemical treatment in this case is the simpler one. Even so, the present tendency is to swing over to distillation of Stoddard solvent, in spite of the fact that it is necessary to carry on this distillation under vacuum in order to make the operation practical.

Carbon tetrachloride may also be purified by the chemical process, although the fact that carbon tetrachloride is twice as heavy per unit of volume as Stoddard solvent, reverses the separation of the solvent and chemical layers, the carbon tetrachloride layer being on the bottom and the chemical solution on top in the clarification system. The chemical treatment of carbon tetrachloride gives no more nearly complete purification than does similar treatment of Stoddard solvent.

Carbon tetrachloride may be completely purified by distillation, and the distillation process is extremely simple.

Distillation of carbon tetrachloride is easy because carbon tetrachloride, as has been said in connection with volatility and odor, is a chemical individual with a definite boiling point, whereas Stoddard solvent is a mixture of chemical individuals and has a wide boiling range; and also because this definite boiling point of carbon tetrachloride is considerably lower than 212° F. so that low pressure, exhaust steam may be used as the source of heat for the distilling operation.

CHART SHOWING BOILING TEMPERATURES OF CARBON TETRACHLORIDE AND STODDARD SOLVENT




The comparative boiling ranges of carbon tetrachloride and Stoddard solvent are shown in the accompanying curves which represent the boiling point of the solvents as the distillation at ordinary atmospheric pressure proceeds. The figures on the horizontal scale show the boiling point temperature in degrees Fahrenheit while the figures on the vertical scale indicate the percentage of the volume of the sample taken which has been distilled. The distillation of carbon tetrachloride is seen to take place over an interval of less than 2° F. while the distillation of Stoddard solvent covers a range of about 70° F.

### DISTILLATION

Further than this, it requires 15 per cent less steam to distill a gallon of carbon tetrachloride than to distill an equal volume of Stoddard solvent. The low distillation temperature of carbon tetrachloride has one other distinct advantage. The fats and oils collected by the solvent in cleaning also have some tendency to vaporize when heated, and this tendency of these foreign oils to distill over with carbon tetrachloride is practically negligible, but may become appreciable in the temperature range required for distilling Stoddard solvent. Distilled Stoddard solvent is more nearly pure than if chemically purified, but distilled carbon tetrachloride may be expected to have an even higher degree of purity than distilled Stoddard solvent.

### HEALTH HAZARD

A great deal of propaganda is being broadcast as to the health hazard connected with the use of carbon tetrachloride. The facts of the matter are that the human body was not designed to absorb any great amount of carbon tetrachloride, Stoddard solvent or any other chemicals than air, water and food. When definite scientific facts are obtained, it will probably be found that the body will not tolerate any greater amount of Stoddard solvent than of carbon tetrachloride. Whatever greater health hazard may be connected with carbon tetrachloride is probably due not so much to its higher toxicity as to the fact that its greater volatility makes dangerous concentration of vapor more likely to be present. As against this fact, however, is the consideration that to be commercially practical a carbon tetrachloride dry cleaning unit must be an entirely closed system; and the losses of carbon tetrachloride in operation must be reduced to a minimum because of its higher initial cost. No system which permits the escape of enough carbon tetrachloride vapor to endanger the health of operators is commercially practical.

It is authoritatively stated that a concentration of 4.8 to 6.7 per cent by volume of carbon tetrachloride vapor in the air may prove fatal after 30-minutes exposure. In order to reach such a concentration, it would be necessary to vaporize from 6 to 8 gallons of liquid carbon tetrachloride in a room 15 x 25 x 10 ft. in dimension and have all of the vapor remain in the room. Such an atmosphere would scarcely be pleasant to the operator and he would have plenty of warning in a feeling of dizziness long before the 30-minute interval had elapsed. If unusual circumstances should allow such a dangerous concentration to develop in a room, and if operators obey the warning of initial dizziness and get out of the dangerous area, it can be quite definitely stated on the basis of years of experience that no permanent injury is likely to result.

### FIRST MADE 90 YEARS AGO

It must be remembered in this connection that while the use of carbon tetrachloride in general dry cleaning is a comparatively recent development, carbon tetrachloride is by no means a new chemical in industry. It was first prepared more than 90 years ago and has been used by various industries for the past 40 years.

### AMOUNT USED

Just when the commercial production of carbon tetrachloride in the United States began is somewhat uncertain but the report of the Federal Census of 1919 indicates a total production for that year in the United States of more than 5,500 ons, 11,000,000 pounds. Since that time, production has been greatly increased and figures for 1930 will probably show between 18,000 to 20,000 tons, approximately 38,000,000 pounds. During these many years of large scale manufacture and industrial use, there has been no general experience among either manufacturers or consumers which would justify the impression that carbon tetrachloride is a serious health hazard. Like many other materials in widespread use, it cannot be handled or dealt with carelessly or without regard for its characteristic properties. If, however, it is handled with

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# AMERICAN DYESTUFF REPORTER

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LOUIS A. OLNEY
Professor of Chemistry and Dyeing, Lowell Textile Institute
Directing Editor

NORMAN ALBIN JOHNSON
Managing Editor

MYRON DREW REESER
Advertising Manager

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## THE GOVERNMENT AND COTTON

THE utter hopelessness of the government taking over a private business enterprise, has again been illustrated by the present condition of the cotton market. The purchase of a large quantity of cotton to relieve an oversupplied market has proven useless. The government is not a commercial organization and can not expect to run a business on a profit making basis. This was rather forcibly illustrated during the war when the railroads were run under government control resulting in a large loss.

Undoubtedly when it purchased the excess cotton crop, the Farm Board had in mind the object of stabilizing the market. But it was not as satisfactory a plan as expected. The Farm Board was not a consumer of cotton—it just meant that the surplus was transferred from one place to another. Now it is still on hand and presents just as much a problem as ever. The Board is anxious to get rid of it as soon as possible at as high a rate as it can command. The cotton growers object to the sale to Germany of the surplus, which the Board has on hand, on the basis that it would remove that market as an outlet to this year's crop. This year's crop has also been characterized as a bumper crop and that means another hugh surplus. This surplus will have to find a market other than the Farm Board this year. They don't want it. In fact if they did take it over it would not improve the basic situation at all—the surplus would still be in existence—as it is now.

The suggestion of the Farm Board that every third row of cotton be ploughed under was certainly not well received. The idea was too far fetched to be accepted. No doubt it would solve the present condition but it would be impossible to get the farmers to agree to do it. The damage has already been done. The best will have to be made of it. If the suggestion had been carried out during the planting season it would have produced a far more favorable condition than that which now exists Whatever the situation is, the cotton interests have brought it on themselves, and they should find the solution to their own problem. That solution is obviously the same as it would be for any other industry—to curtail the amount of production. Governor Long of Louisiana offers a simple plan which would prohibit excess planting of cotton. Any well organized and well managed business would dispose of their own problem by a systematic method of planning. Why not have the cotton growers do the same?

The purchase of the excess cotton supply was merely delaying a readjustment of the system of cotton growing. As long as the growers could get rid of their product they continued planting in large amounts. Had the Farm Board not interfered the cotton interests would have had to seek their own salvation and the period of readjustment would be under way. Had it been necessary for them to retain their previous surplus they would not probably have as large an excess this year.

There is no doubt that the Farm Board can assist in the situation, as it has done previously, but they should leave the ultimate production and marketing problems to the grower.

According to C. T. Reeve in Mund and Winslow's cotton review, surplus has piled up "therefore, not because of underconsumption, not because of overproduction, but because of underconsumption resulting from world-wide economic dislocation, and partly, as we ourselves believe, to obstructions in the nature of Governmental price control operations."

Naturally with underconsumption even normal production would mean a surplus resulting in lower prices. It would be as well for the farmers to take their price loss at the time the surplus occurs as to have it delayed for a year or two—with the surplus increasing in the meantime.

The fact still remains, however, that the government is not organized for carrying on commercial enterprises, and such are most sensibly and profitably left to private interests. The government can always help by worthwhile and constructive criticism but their scope should be limited.

## SIMPLIFICATION AND ELIMINATION OF WASTE

A STATE-WIDE simplification and elimination of waste, among Pennsylvania producers, distributors and consumers, is to be sponsored by the Pennsylvania State Chamber of Commerce, with the active assistance of the Division of Simplified Practice of the Bureau of Standards, Department of Commerce, according to George K. Burgess, Director of the Bureau.

The Department of Commerce at Washington has been dealing with this matter for about ten years, having been started by President Hoover at the time he was occupying the position of Secretary of Commerce. The Chamber of Commerce of the United States working on a nation-wide basis has been cooperating extensively since the inauguration of the plan.

Recently it was decided that simplification might very well be taken up on a state-wide basis by state chambers of commerce. Such a campaign has been in effect during the past two years in the State of California and for the past year in the State of Washington. The results in these two states have justified placing the plan on a state-wide basis.

The state chambers of Ohio and Pennsylvania have been recommended by the United States Chamber of Commerce to the Department of Commerce as two chambers where this work could be taken up and put forward on a state-wide basis.

In Pennsylvania a special planning committee has been appointed to direct this activity and one of the staff men was appointed to give special attention to the development of this work. The work will not be started until the planning committee has outlined a definite procedure in cooperation with the Department of Commerce. The campaign will be developed through three stages: first, general education as to the philosophy of simplified practice and the building of interest by local applications of this principle; second, acceptance of existing simplified practice recommendations by Pennsylvania organizations; and third, initiation of new simplified practice recommendations at the suggestion and request of Pennsylvania organizations.

There are, then, four states in which a campaign of simplification and waste elimination is now under way. The two states wherein the plan has been functioning for some time have shown effective results. If the plan works out well in Ohio and Pennsylvania, there is no reason why it should not be adopted by other states. Simplifying practices and elimination of waste will mean a distinct saving to the industrial organizations within the states. The feature of the program which includes the suggestion of recommendations by the concerns themselves should insure their cooperation.

Waste elimination has always been a big factor in industrial circles. Such elimination may be made a source of profit to the industries involved. Whatever the outcome may be, it will prove interesting to watch the development of the plan as now started in Pennsylvania.

## Winter Colors

Nine new colors for winter have just been sent out to members of the Textile Color Card Association in confidential swatch form, it was announced recently by Margaret Hayden Rorke, managing director. The 1931-32 Winter Color Card showing these shades will be issued shortly.

The newest color developments in fashion will be portrayed on this mid-season card, including certain shades high-lighted at the recent Paris openings.

Smart renditions of red are significant among the new colors. Bagdad Red is a rich terra cotta tone, while Brique, a darker shade, is a new version of rust red. Tomato Red is a clear, animated hue of yellowish cast.

There are two outstanding interpretations of green. Persian Lime, the color of the exotic fruit by that name, is a subtle yellowish green of olive tonality. Hollywood Green is a bright, vibrant hue of importance for sports and evening wear, as well as an accent note with brown or black.

Brown, which retains all of its style significance, is represented in Sultana Brown, a rich, deep shade with a suggestion of mauve. Paris Beige, slightly rose-tinted, is a smart complement to brown, as well as a contrasting note with black, green, red or rust. Another lighter shade, especially adaptable for combination with brown or black, is Persian Gold.

A new fashion note is introduced in Empire Purple, a rich hue reminiscent of the court life of Second Empire days.

It was stressed by Mrs. Rorke that the new colors supplement the 1931 Fall Season Cards, and in no way lessen the importance of the latter, nor detract from the style value of the basic colors for fall and winter adopted by the Color Coordination Committee of the National Retail Dry Goods Association, and sponsored as well by the Industrial Council of Cloak, Suit and Skirt Mfrs., the Associated Dress Industries of America and the Allied Millinery Associations.

## 1933 World's Fair

Plans by which the textile industry may exhibit its products to the millions of visitors to Chicago's 1933 World's Fair, portray its processes of manufacture and dramatize the evolution of the industry are now being considered by a number of leading units in the industry.

All branches of the textile industry, including silk, wool, cotton, rayon, mixed cloth, carpets and fabrics of all descriptions will, it is expected, be represented in the Exposition.

The history of the textile industries in the last century, it is pointed out, illustrates the theme of A Century of Progress Exposition. The 1933 World's Fair will seek to show how the world has been improved and the living conditions of the average citizen bettered through the commercial application of scientific discoveries and inventions to industry in the last hundred years. In this period, the introduction of improved machinery, the use of steam and electricity, and the perfection in fabricating processes due to scientific research and inventions have transformed the textile industry. As a result, textile products which a century ago were unobtainable luxuries are now commonplace necessities with the average person.

## Hydron Blue RR

The General Dyestuff Corporation has sent out a circular of Hydron Blue R R Powder which corresponds in fastness properties to Hydron Blue R, but is said to be more brilliant and redder in shade.

# Technical Notes from Foreign Sources

## Tannin in Textile Work

*Dr. W. Dahse—Faerber-Ztg.* 67, 57 (1931).—In spite of the long-continued and widespread use of tannin in dyeing and printing, only certain general facts about it are known, and a great many detailed points regarding its properties and uses still await discovery or explanation. The different forms of tannin, powder, needles, heavy crystals, and the almost chemically pure form called foam, are further divided by the manufacturers into series of brands and grades for special purposes; they vary in tannin percentage, color, and solubility, they are adapted for dyeing in delicate, medium, and dark tones, and for printing in pure whites with sharp outlines for delicate work, for medium tones and sharpness of outline, etc. For determination of their value, the textile chemist has to depend, for convenience, upon comparative trial dyeings. For example, according to Heermann, 0.5 g. are dissolved in hot water, made up to 500 cc., 10 g. of sodium chloride added, and a 10 g. skein of cotton yarn, well boiled out, mordanted in the solution during a 3-hour cooling-off. Each skein so treated (in baths of different tannins) is then strongly wrung out without rinsing, immersed in a bath of 200 cc. of basic iron sulphate or pyrolignate, of about 1°-2° B., and worked in this bath for 15-20 minutes. The skeins are then rinsed and dried, and the strength and suitability of the tannin decided from the depth of the color. To test a tannin for its value for light tones, the cotton yarn is mordanted in the same way, fixed with an antimony salt, and dyed in suitable light-tone baths of basic dyestuffs, as Fuchsine, Methylene Blue, etc.

The process which goes on, in relation to the tannin, during the process of dyeing, is more complicated. According to Weiss, the degree to which the tannin is taken up by the cotton reaches an equilibrium between the concentration of the tannin in the fiber and in the bath. Whether a definite chemical compound is formed by the customary treatment with an antimony salt, is not yet known, nor do we yet know the optimum temperature for the mordanting and fixing process, although it apparently lies somewhere around 50° C. According to Sunder, antimony tannate, with excess of tannin, easily forms colloidal solutions, through which condition the lack of levelling, and fastness toward rubbing and washing, of the dyeings is explained.

The natural sources of tannin, sumach, myrobalans, divi-divi, gall-apples, etc., are sometimes drawn upon directly to produce a tannin-liquor, but, as their content in tannin varies so greatly, it is better to use a commercial tannin of known strength and purity.

Tannin finds most use in connection with the application of the basic dyestuffs, in direct cotton printing for the light mode-tones, such tones being easily produced. Those dyestuffs which are free from zinc chloride are generally used, either as the pure hydrochloride or as the color-base, which is gotten into solution by organic acids, formic, acetic, tartaric, or derivatives of them, such as acetine, etc. The zinc chloride double salts of the dyestuffs would cause damage to the fabric when the dyed goods are steamed. In reference to the organic acids just mentioned, Liepatoff, Jamenkowa, and Liepatoffa have found that they decrease the affinity between dyestuff and fiber, and that it is better to use neutral organic solvents in presence of substance which will neutralize any acid set free during the process of dyeing.

In discharge printing with tannin as a mordant, when the goods prepared with tannin or a tannin-antimony compound are printed with a caustic paste alone, or with one containing also basic dyestuffs, complaint is often made that the strong caustic, ultimately at least, damages the rolls, doctor-blades, etc. W. Sieber avoids this source of trouble by use of a special gum-preparation for a thickening-agent: 20 liters of gum Senegal solution, 2/1, are slowly treated with 53.5 kilos of caustic liquor of 36° B., with good stirring and cooling, keeping the temperature below 22° C. For tannin padding-baths of a strength of up to 20 g. of tannin per liter, the above thickening-agent may be cut 1-1 or 2-1, using gum Senegal solution of 3-5 for the diluting agent. If the amount of tannin is to be appreciably higher and the discharge to be more effective, the above caustic solution (53.5 kilos) may have a further 1700 g. of caustic potash dissolved in it before it is added to the gum Senegal solution. In the case of reserve-printing with insoluble azo colors, beside the common reserve with tin compounds, sulphites, and persulphates, tannin is of great use, especially if employed in conjunction with non-volatile organic acids. In direct printing with tannin, the basic dyestuffs in general give faster dyeings than is the case with other fixing agents, because the color-lake enters the fiber only during the process of steaming, and is then fixed. In the ordinary printing processes, an excess of antimony salt acts as a precipitant for the color-lake, while excess of tannin or antimony-tannin compounds, especially the colloidal ones, have a solvent action upon the color-lakes. In the former case, the dyeing is more upon the fiber, and so is easily rubbed off; in the latter case, the dyeing is within the fiber, and so is faster to rubbing, and quite probably to light and washing as well.

Various efforts have been made, of course, toward a more specific improvement of the fastness-properties of tannin-printed goods; consisting in either addition of, or

after-treatment with, such substances as thio-urea, sodium meta-phosphate, glucose, copper-oxide, Turkey-red oil, and such substances as phosphotungstic acid (of which more below). Wosnessensky has proposed the addition of resorcinol for improvement of the fastness to light and washing. He carried out parallel experiments, using printing-pastes containing basic dyestuffs, acetic acid, and tannin, with resorcinol, and colors in which the acetic acid was replaced with phenol. The goods were steamed for an hour, and the colors fixed with tartar emetic. Some improvement was attained. Increased fastness to rubbing is attained, according to German Patent No. 308,815, if the process is carried out by printing with a paste containing, e.g., Methylene Blue, resorcinol, tannin, acetic acid, and warm water, then steaming, passing through a bath of antimony salt, and rinsing. Another procedure adds the tartar emetic directly to the paste, in which case steaming and rinsing complete the process. The thickening agent is starch paste. German Patent No. 371,597 proposes the addition of chloracetic acid or glycollic acid to the paste; by this method, simple drying, without steaming, fixes the color; and it is claimed that a higher degree of fastness toward water, washing, and rubbing is attained. The procedure may be given in detail:— the goods are printed with a paste composed by dissolving 1 g. of basic dyestuff and 5 g. of acetic acid in 20 cc. of boiling water, adding to this solution 52 g. of tragacanth-starch thickening, and 2 g. of tannin; when the last substance has dissolved, 20 g. of chloracetic acid are added. The goods are printed with this paste, dried without steaming, passed through a cold or lukewarm tartar emetic bath, which contains 10 g. of tartar emetic to the liter, and the goods then rinsed and soaped. (Instead of the 52 g. of thickener and 20 g. of chloracetic acid, 42 g. of thickener and 30 g. of glycollic acid may be employed.) A dyeing bath with these assistants would be composed of 1 g. of basic dyestuff, 5 g. of acetic acid, these dissolved in 20 cc. of boiling water, then 42 cc. of cold water added, 10 g. of tragacanth-starch thickener added, 2 g. of tannin, and, when this has dissolved 20 g. of chloracetic acid. As soon as the chloracetic acid has dissolved, the piece goods are padded in this bath, and squeezed at such a pressure that a gain in weight of 100% is reached. The goods are then well dried, and, without steaming, passed through the usual bath of tartar emetic, then rinsed and soaped. (Instead of the 20 g. of chloracetic acid and 30 cc. of water, 30 g. of glycollic acid and 32 cc. of water can be substituted.)

This patent is held by Geigy. It involves two supplementary patents, of which one, No. 386,032, claims to increase the fastness-properties by employment of a printing paste which differs from the one already given by substitution, for the 20 g. of chloracetic acid, 10 g. of 83% phosphoric acid and 10 g. of chloracetic acid (the acetic acid already referred to is apparently one of 40%). The subsequent operations are as given above. The other supplementary patent prescribes for a printing paste one of 1 g. of basic dyestuff, dissolved hot in 32 cc. of water and 4.5 g. of 80% acetic acid, 10 g. of ethylene glycol, 2.5 g. of tannin, and 50 g. of starch-tragacanth thickener. For a dyebath, 1 g. of basic dyestuff is dissolved hot in 32 cc. of water and 4.5 g. of 80% acetic acid, 10 g. of ethylene glycol, or thio-diglycol, 2.5 g. of tannin, 40 cc. of water, and 10 g. of starch-tragacanth paste. In each of these recipes, after printing or dyeing, the procedure is as before, i.e., drying well, passing through a bath of 10 g. of tartar emetic per liter, rinsing, and soaping.

The fastness to rubbing of basic dyeings can also be increased, according to German Patent No. 471,788, if the tannin-mordanted goods are first treated with a solution of an alkali salt of tin or aluminum, or a silicate, and then with a solution of the acetate, formate, lactate, tartrate, or sulphate of aluminum, and then dyed in an acid-free bath, which has been made up with addition of a solution, prepared in the heat, of a mixture of about 3 parts by weight of some albuminous substance, as casein, about 2 parts of a borate (alkali or ammonia or both together), and about 5 parts of an inorganic or organic ammonium salt. The goods should be entered at about 50° C., the temperature slowly raised to boiling, and the bath kept at a gentle boil for about ½ hour, after which it is allowed to cool to about 60° C., and the goods then rinsed. This casein mixture, prepared as above, should constitute about 5-15% of the weight of the goods, depending upon the depth of shade of the dyeing desired.—Another method of increasing fastness to rubbing is given in German Patent No. 485,894, and consists in employing as dyestuffs the lakes formed from basic dyestuffs or their sulphonic acids, and complex metallic salts; these lakes being dissolved or suspended in an organic medium, and fixed upon the fiber either with or without additions to the bath, as may or may not be necessary.

The complex metallic salts just referred to appear to have attracted much interest in this connection; cotton treated with a solution of sodium phosphotungstate and a 10% aluminum sulphate solution, dried, and then printed, giving results of excellent fastness. Of the procedures useful for such premordanted cotton, the following will serve as examples:—

1—20 g. of Victoria Blue B, 50 g. of acetic acid of 6° B., 200 g. of water, 630 g. of gum thickening 1/1, as a paste, printed upon the mordanted goods, which are then dried, and the color fixed by steaming. Instead of the goods being mordanted with phosphotungstic acid, other hetero-poly-acids, such as phospho-molybdic and silico-tungstic acids, etc., or their mixtures, can be used. Other dyestuffs similar to Victoria Blue may also be used.

2—2 kilos of cotton yarn are mordanted by one hour's immersion in a solution of 500 g. of sodium phospho-tungsto-molybdate in 25 liters of water, then wrung out and dried. The skeins are dyed in a 2% bath of Diamond Green GX for ¾ hour, at 60°-80° C.

3—Cotton or silk is printed with a paste prepared by dissolving 40 g. of the phospho-tungstic acid lake from Rhodamine 3G extra, in 460 g. of pyridine, the solution being mixed with 500 g. of starch-tragacanth thickener made acid with acetic acid. After drying, the printed

goods have the dyestuff fixed by steaming, and are then cooled and lightly soaped. In place of pyridine, other solvents, such as thio-diglycol, ethylene chlorhydrine, etc., may be used. Also, lakes from other basic dyestuffs, including thse containing sulpho groups, may be used, either phosphotungstic or similar complex acids or salts or mixtures of them being employed for the mordant or precipitant.

In general, the difficulties encountered in getting good results with the use of tannin mordants, particularly the occurrence of streaky dyeings, are mostly due to the use of too strong a tannin bath. Spotty dyeings are generally due to the mordanted goods having been allowed to dry partially before the treatment with the antimony bath.

In employing sulphur dyestuffs for printing, the chief difficulty lies in the action of the sodium sulphide upon the copper rolls, the conversion of the surface of the rolls to copper sulphide at once diminishing the sharpness of outline of the engraved design, and ultimately shortening the life of the roll through flaking off of the brittle sulphide, or through damage by accidental rough handling producing serious scratches, etc., which can happen much more easily with a brittle substance like the sulphide than with the pure copper surface. By purifying the dyestuff from the sodium sulphide at least frequently present in it, and by adding to the printing paste various substances which combine with and render harmless the sulphide of the reducing bath, this detrimental action can be to some extent diminished, but the dyestuff does not then exhaust well. Substitutes for sodium sulphide, such as Rongalite, glucose, stannous oxide, etc., have been proposed. But Justin-Miller has suggested employing lakes prepared by action of tannin upon the leuco-derivatives of the sulphur dyestuffs (his idea is based upon the observation of Kurz, that tannin forms a stable compound with indigo-white). The compounds formed from tannin and the leuco-compounds of sulphur dyestuffs are much less prone to oxidation than are the reduced dyestuffs alone. If, instead of tannin alone, a metallic salt which forms with tannin an insoluble compound (zinc sulphate, tartar emetic) is used in conjunction with it, the precipitated compound carries down with it the leuco-derivative of the sulphur dyestuff, and this precipitated substance is so stable that it can be dried without suffering oxidation in the air. Immedial Indone R, the dyestuff with which he chiefly worked, forms a derivative which is pale grayish-blue in color. If this lake is stirred up with caustic, it is decomposed, and on being filtered and washed is oxidized at once to the dyestuff originally reduced. Experiments carried out with this tannin-leuco-derivative as a printing color have shown that stable preparations can be made up, which are not decomposed by steaming the goods for one hour, but require for their decomposition a treatment with caustic soda, which removes the tannin as gallic acid (in the form of its salt). The method seems promising enough to deserve further study, and extension to the sulphur dyestuffs in general.

### Wash-Liquors and Loss of Soap

*R. Kring—Monats. f. Textil-Ind.* 46, 57 (1931)—(*Abstracted from Seifensieder-Ztg.* 1929, p. 285).—The author refers to the belief that, to avoid loss of soap through precipitation when hard waters are used, an addition of soda or water-glass will render the calcium or magnesium salts, which are the cause of the hardness, harmless, and states his opinion that these additions are totally useless for the purpose, on account of the great dilution at which they should ultimately come into reaction. He adds that sodium perborate is likewise useless for the purpose. A detailed discussion of the subject explains his reasoning.

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### Methylene Blue Upon Wool

*E. Ristenpart and H. Schwerdtner—Monats. f. Textil-Ind.* 46,28 (1931).—The first part of a paper upon the general reaction between fiber and dyestuff.

It was A. Kertecz who in 1919 pointed out that damaged parts of wool fiber could be detected by dyeing the fiber in a bath of Methylene Blue acidified with acetic acid, at 50° C., the damaged part giving a deeper tone than the undamaged. C. Kronacher and G. Lodemann in 1926 stated that the yellowish tips of scoured wool were dyed more deeply after 15 minutes than were the basal ends, and assumed that the tips had suffered in some way. Definite work has been done also upon the detection of oxycellulose in cotton by the same method. But exact knowledge of the general behavior of the dyestuff toward wool needs further supplementing. This first part of the paper deals with certain experiments which have been carried out by the authors upon the topic.

The first series of dyeings was carried out with Methylene Blue MD in the following concentrations: 0.25, 0.0625, 0.0156, 0.0034, and 0.00097 g. of dyestuff per liter, and with 0.0, 0.0186, 0.075, 0.3, and 1.2 g. of acetic acid per liter with each of the above dyestuff percentages. The amount of material, Zephyr A, was 50 m. = 3.125 g., in 750 cc. of bath, dyeing for 20 minutes at 50° C. None of the baths were exhausted. The results showed, of course, that the depth of tone increased with the percentage of dyestuff, but also that it decreased with an increase in the acetic acid content. The amount of dyestuff chosen by Kronacher and Lodemann (1 g. per liter) is too great, unless the amount of acetic acid is equally high. If too little acid is present, the dyeings are hopelessly uneven; if no acid be added, the method may be of some use for microscopical tests, but not for dyeing studies. The middle percentage employed in the series, 0.0156 g. per liter, is only slightly higher than that chosen for the test of oxycellulose in cotton (0.01 g. per liter). This series was therefore run through again, but with quantities of acetic acid varying from 0.0 to 0.2 g. per liter. The most favorable amount for a good test was the middle figure, 0.0125 g. per liter. It is proposed, therefore, that the procedure of Kertesz be modified to conform to the percentages now customary for the oxycellulose test (0.01 g. of dyestuff and 0.01 g

of acetic acid per liter), in order to simplify matters by using the same bath-strength for either wool or cotton.

The question may properly be asked—could a damaged condition of the wool be detected by such a dyeing test? Wool successfully dyed is of course out of the question, which would relate only to undyed, especially to bleached, and more especially to material bleached by an oxidizing agent, since reducing agents do not harm wool. And still more especially, we should consider wool subjected to oxidative bleaching above the ordinary temperature; i. e., by the hydrogen peroxide method. This reagent acts more powerfully, the more alkaline the bath. Most procedures direct that the bath be made just alkaline with ammonia. There seems to be no information in the literature as to the degree of alkalinity which gives the most effective bleaching with the least damage to the material. The authors have found that a bath of hydrogen peroxide (they used a bath of 3% peroxide), containing an amount of ammonia (reckoned as $NH_3$) equal to 3% of the peroxide used, gave maximum bleaching, and that the Methylene Blue test afterward showed no deeper dyeing of the fiber than was the case with baths containing less ammonia. With more than 3% of ammonia, the fiber showed a slight degree of yellowing. With this optimum-condition in mind, the authors attempted to bring about damage to wool fiber by parallel treatment with the optimum bath, and with a bath containing the ammonia, but not the peroxide. The fiber showed damage, but no loss in weight, the damaged portion being converted to a tenacious, slimy substance, which remained upon the undamaged part of the fiber. The authors incline to the belief that the term "damage" is not properly used, if it implies loss of tensile strength or elasticity, since the Methylene Blue test shows only an alteration in affinity between fiber and dyestuff, which means only chemical, and not necessarily physical, alteration.

### Immunized Vegetable Fibers

*German Patent No.* 451,641 (6/*XI*/'23) (*released* 29/*X*/'27)—*L. Cassella and Co.*—The particular purpose of the process specified is not for printing, but for immunizing in bulk, in order to produce yarns for effects in piece dyeings. The older process (G. P. No. 346,883) consisted in immersion of the fiber, previously treated with some alkaline agent, in a solution of an aromatic acid chloride. This present improvement consists simply in the addition of soaps, or of Turkey-red oils of easily soluble nature, to the alkaline pretreating bath. Results are claimed to be much better. The example given cites treatment of cotton yarn in a caustic potash bath of 19°B., in which 2.5% of potash soap containing about 40% of fat (fatty acid) is present, wringing out thoroughly, and treating the yarn in a solution of benzoyl chloride in benzene, according to the earlier patent.

### Acetate-Silk in Dry-Cleansing

*Dr. A. G.—Faerber-Ztg.* 66,1003 (1930)—The increasing use of acetate silk in modern solid and mixed weaves has made it necessary to pay more attention to the characteristics of the fiber than has heretofore been the case. In dry-cleansing goods composed of or containing acetate silk, for example, preparations sold for domestic use in cleansing—"spot-removers"—apart from their probably efficient effect in removing the spots desired to be removed, will also have a harmful effect upon the fiber, if they are composed of or contain any substance which will dissolve or even seriously swell acetate silk; i.e., the spot will be removed, but a worse spot will be caused by the preparation. Chloroform, for example, so often an ingredient in these spot-removers, which are "sold by the bottle," is dangerous to acetate silk. The artificial silk industry has hardly as yet attained the manufacture of an acetate silk which is really chloroform-insoluble—really and fully so. Technical chloroform, and this is probably what is used most often in commercial cleansing compounds (the manufacturers of such compounds could hardly be expected to pay the much higher price demanded for c.p. chloroform) generally contains some alcohol, acetone, etc., and these two substances are capable of working great harm to the acetate silk. An acetate of cellulose truly insoluble in chloroform is possible, but is a substance found only in the laboratory, as incidental to research. The truth is, that the use of dry-cleansing agents upon acetate silk is really a dangerous procedure.

In dyeing and finishing, as in dry-cleansing, we have to reckon with the great variability in the properties of acetate silk. Wool, natural silk, and cotton may be considered as fairly uniform in composition and behavior—the statement appears odd, when, e.g., the variable sulphur content of wool is considered; but it is true, none the less, that the natural fibers are characterized by a general uniformity of behavior which, in the case of wool, at least, is really very surprising. Silk shows a general uniformity not unexpected, considering the only slight variability which exists in the insect species from which it comes, and the uniformity of the diet upon which the silkworm is fed. Cotton is almost absolutely uniform in behavior. Viscose, as regenerated cellulose, might also reasonably be expected to range itself with natural cotton. But, in the case of acetate silk, the reactions involved, of acetylation and hydration, proceed with a strange irregularity, though it is better to say that the processes are extraordinarily sensitive to minute variations in conditions. The kind of acid used, the amount of water present, and the length of the acetylation-process all affect the nature of the final product formed, though the producers have learned how to control the factors within rather broad limits. But the product as we know it is of variable behavior.

One decided difficulty in the use of solvent cleansing agents is, that in some cases the different components of the mixture have little or no effect upon acetate silk when used alone, but that in mixture they do swell, or partly or wholly dissolve, the artificial fiber. Damage resulting is not necessarily evident by change in elasticity or tensile

strength, or by wrinkling of the goods; an absolute criterion is an alteration in the coefficient of refraction as observed on the surface of the goods after treatment with the cleansing agent. Such a change in the cleansed area does not consist of a "spot," in the sense of the cleanser, but is such a misfortune in the eyes of the customer, for it means, not a differently-colored spot, but a spot of a luster noticeably different from that of the surrounding area.

Laboratory study of cleansing problems does not give an altogether satisfactory view of the situation. Experiments are generally made, not upon a whole garment or upon a good-sized sample of the material, but upon comparatively small samples of the goods, with which it is much less easy to detect any alteration of surface luster in the locality of the removed spot, than is the case when a whole garment is actually being worn upon the person. Another point worth remembering (in other case beside the present) is, that the reagents employed in the laboratory are generally pure or nearly so, whereas the solvents used in practical work are almost never of a purity at all approximating to that of the laboratory reagents.

Commercial cleansers are advised never to guarantee results when the goods contain, or consist of, acetate silk; in their preliminary experiments, to use solvents of a high degree of purity; to let the cleansed spot dry out thoroughly before coming to any conclusion as to the usefulness of any particular solvent; and finally to use solvents as pure as those found satisfactory in the tests. These points make reasonable, of course, a considerably higher charge for services.

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### Sources of Trouble in Mercerization

*G. H. Faerber-Ztg.* 66,596 (1930)—Simple as the process of mercerization is, and simple as is the equipment necessary for its carrying out, it is a process requiring an astonishing amount of experience and skill. If a lot of cotton yarn is improperly mercerized, the defect is not perceptible until the material comes to the dyeing; for example, let a large lot of yarn be improperly mercerized, and knitted into, say, some hundred dozen of stockings. These stockings, when dyed, do not dye evenly; the mercerization was streaky, and this condition in the yarn could not be detected at that point. Such poorly dyed stockings will sell at only one-half to one-third the price which properly dyed articles would bring, and the mercerizer, upon whom the blame ultimately comes, also loses his customer. Worse still, let such material be used in the knitting of silk stockings, in certain parts, say the foot, etc.; the same amount of damaged yarn will then depreciate the value of an enormously greater amount of much more costly articles. Yet the original cause of such trouble and loss will lie in the neglect of perhaps one little precaution in the mercerizing process.

Before the yarn goes upon the machine, it absolutely must be perfectly wetted out, most certainly by means of one of the modern wetting-out agents, among which the preference will be for the one which acts rapidly and powerfully, and is stable toward hard water; for the precipitation of a lime soap upon any part of the yarn will hold back mercerization of the covered portion. Material ineffectively wetted-out at this point may, by longer and special treatment, be finally dyed level. But the action of the caustic is so brief in duration, that imperfect penetration will most probably lead to non-level dyeing, whether the imperfect penetration is due to insufficient wetting-out, or to deposition of lime soaps from hard water. The next point requiring care is the wringing or squeezing out or centrifuging of the wetted-out material. If this process is imperfectly carried out, the water left in the yarn will dilute the caustic to below the point at which mercerization will satisfactorily take place, either generally through the lot, or, still worse, locally. In any case, the optimum concentration of the caustic should be kept up at all points, by providing means for keeping the caustic liquor in constant circulation, and by addition of fresh strong caustic as the concentration of the bath falls. If the yarn is unequally wet, i.e., not thoroughly wrung out or centrifuged, the degree of mercerization will vary from point to point in the lot, according to where it is more or less wet from the wetting-out process.

Even very slight variations in the concentration, and also the temperature, of the caustic, bring about corresponding variation in the degree of mercerization, out of all proportion to the magnitude of the variation. The duration of the process appears to be of not so great influence; the time allowed usually is really rather brief, and is not sufficient for complete mercerization, through and through, of all yarns. The tension to which the yarn is subjected is, however, of much importance. In raw stock, the length of skein is already set, and is taken into consideration, the stretch being calculated to compensate for the shrinking which always accompanies the process. But every part of the same lot must be subjected to the same tension.

After the caustic bath, the material is washed twice, first with warm water (the ideal temperature is 40° C.), then with cold water. Different parts of the same run must be washed at the same temperature as closely as possible. At this point, the working of the material upon machinery usually ends. If the material is to be bleached, it goes to the bleacher, still wet; if it is to be dyed directly, it is almost always dried, since in the freshly-mercerized, wet state it possesses too high an affinity for the dyestuff, and so runs the risk of dyeing unevenly. Even for blacks it is best to dry the goods first, for otherwise the dyebath will become exhausted, and the loading of the fiber with dyestuff will produce a dirty, brownish black. When the washed yarn is to be dried, since two washings will hardly remove all the caustic, the material is treated in an acid bath containing 2 g. of sulphuric acid in the liter, for about 15 minutes, and then again washed, this time in cold and in warm water. Instead of the last, the warm, washing, a bath containing a little ammonia may be substituted; the point is, to remove all

free acid before the drying. The effectiveness of the acid treatment and the final washings is best followed up by frequent titrations of the washwaters. The drying, following the final washing, is, again, not regarded seriously in some quarters; yet it is of great influence upon the results, whether the goods are dried at too high or too low a temperature, or whether under tension or not. The temperature of drying affects the affinity of the material for the dyestuff. The question of tension affects the luster of the yarn, for the luster increases as the tension during drying, while the affinity for dyestuff decreases as the drying-temperature rises. We have little precise information about these two points, temperature of drying and tension during drying, and it is unfortunate that more than one cause of failure cannot be traced down, because these factors have been considered as unimportant, and so have been ignored during the study.

The process of mercerization requires, and deserves, the same careful attention to every point, which we voluntarily give to, say, the process of dyeing the vat colors. But it has not, as yet, largely received this attention.

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**Benzine vs. Carbon Tetrachloride in Dry-Cleansing**

*Dr. A. F. G. Segitz—Faerber-Ztg.* 66,118 (1931).—Benzine is still largely used in dry-cleansing establishments. In spite of its inflammable nature, and the explosiveness of its vapor when mixed with air, accidents due to its use appear to be not more frequent than is the case in ordinary industrial plants of other natures; and this fact appears to have its appeal to the conservative spirit of the industry, although in carbon tetrachloride there is available a solvent which is far more effective per se, and is also absolutely non-inflammable. Benzine is not only dangerously inflammable, but its vapors are decidedly prejudicial to health, sometimes fatally so. The idea prevails in some quarters that it is benzene ("benzol") which is harmful to health, and not benzine; that the worker, after preliminary symptoms of dizziness, numbness, and headache, becomes immune to the effects of benzine. Such cases of acquired immunity do exist, but in general the substance acts as toxic to the nervous system, and, if allowed to exert its influence steadily for any length of time, produces disorders of the circulatory and respiratory system, rapid pulse, loss of control over the excretory exist, and ultimately destruction of the epidermis. The inhalation of benzine vapor accomplishes all this; the danger from accidental swallowing of the fluid is much less. The subject has been carefully studied by Prof. Dr. K. B. Lehmann of Wuerzburg.

Occasionally, to enhance the solvent properties of benzine, some aromatic hydrocarbon, as benzene, is added. This also seriously enhances the toxicity of the vapors, and makes effective ventilation of the premises all the more necessary.

As to the physiological effects of carbon tetrachloride, it must be admitted that this, and similar substances, also exert dangerous influence upon health if the vapors are persistently inhaled; again, the heart and lungs are the parts chiefly affected. Yet, for various reasons, there are many fewer cases known of health being prejudiced through its use. Its vapors are heavy, and ordinarily sink to the floor and pass away outdoors without much danger of reaching the height of the workers; and, on account, perhaps, of the great volatility of tetrachloride, its high specific gravity, and cost, it is usually employed in closed apparatus instead of in open vessels. Benzine vapor, if present only to the extent of 1.9-5.3% in the air, forms an explosive mixture. Sometimes benzine is mixed with tetrachloride, one to two, or less, the mixture giving off a non-explosive vapor (the influence of tetrachloride vapor in comparatively small quantities as a "depressant" toward combustion is well known). The factors which may give rise to benzine vapor explosions, the spark of an electric switch, a sparking motor commutator, the breaking of a lighted electric bulb, the scraping of a hobnail upon a nail in the floor, a furtive cigarette, etc., are perfectly obvious. In addition, however, benzine is one of those liquids which by mere agitation may become electrically charged; a wool or silk garment, worked about in benzine and simply withdrawn quickly, may produce such an electrical charge, in solvent and garment, that upon the garment being withdrawn from the bath, an electrical discharge ((a static spark) may pass between it and the surface of the liquid just as it is leaving the liquid, with consequences easily to be imagined. In the cold, dry air of winter, this danger is especially great. As a good quality of benzine is a good non-conductor, grounding the metal tank which contains it will probably do no good.

It is difficult to see why the users of benzine mostly still stick to the old-fashioned open vessels, while those employing tetrachloride seem to incline toward scientifically constructed, closed apparatus. Were such machinery used for benzine, almost the only factor in disfavor of benzine would be its inferior solvent action, which might be compensated for by its comparative cheapness allowing greater quantities to be used.

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**Hercules Chemists**

Three Hercules Powder Company research chemists have returned from Germany to the company's headquarters at Wilmington within the past few weeks. They are: Dr. E. J. Lorand, Dr. H. M. Spurlin, and Dr. Kyle Ward, Jr.

For the past two years, the Hercules men have been studying cellulose problems in Berlin. Dr. Lorand and Dr. Ward have been at the University of Berlin working with Prof. Hans Pringsheim, and Dr. Spurlin has been at Kaiser Wilhelm Institute studying with Prof. Herzog, both professors being well-known cellulose authorities.

The higher fatty acid esters of starch and cellulose, osmotic pressure measurements of cellulose solutions, and new methods of degradation of cellulose have been the main research problems undertaken by the Hercules representatives.

## SAPONIFICATION TREATMENTS FOR CELLULOSE ACETATE RAYON

(Continued from page 586)

it is possible to use either a carbonate (for example potassium carbonate) or caustic soda or caustic potash. The answer to this question must depend on the purpose to which the rayon material is afterwards to be put, and also on whether it is the handle or the resulting dyeing properties which are most important. The choice of method will be guided by the facts that saponification by potash gives the softest handle whilst saponification with caustic soda gives the greatest affinity for dyes.

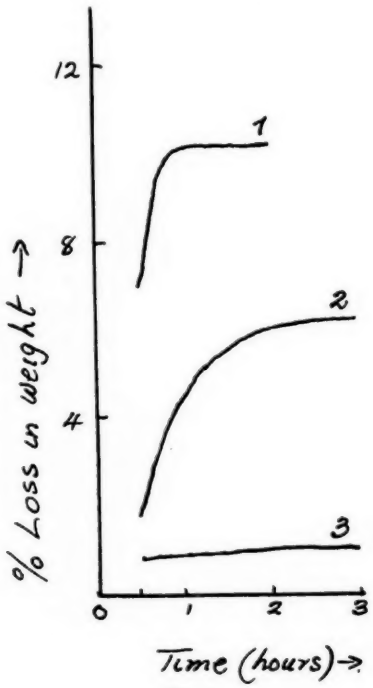


*Fig. 4*

It is also of some importance to know the efficiency of the saponification process. A concentration of alkali or a temperature of saponification should be employed by which the greatest proportion of the alkali used actually effects saponification. In Fig. 3 is shown the efficiency of saponification as obtained (with barium hydroxide) using increasing initial concentrations of the alkali; it is evident that too weak an alkaline solution should not be used since in this case only a small proportion of the alkali will enter into the reaction. The efficiencies for other alkalis such as caustic soda and potash would have to be determined by those wishing to use either of these alkalis, but in this connection the curves in Fig. 4 which were obtained with caustic soda by Coltof, Waterman, and Wolf (*supra*) will be of assistance.

In conclusion it is pointed out that by partial saponification of cellulose acetate rayon it is possible to make dyeing easier and often cheaper, and also to improve certain properties of the rayon, but particularly its resistance to hot ironing; these benefits can be secured without deleteriously affecting its luster or softness of handle. For these reasons it is believed that saponification processes should not be neglected so much as they have in the past.

## CHEMICAL AND PHYSICAL PROPERTIES OF CARBON TETRACHLORIDE

(Continued from page 598)

simple and reasonable precautions, no unfavorable effects on health need be anticipated.

### Summary

In conclusion, the various points of comparison developed above may be briefly summarized as follows:

1—*Cleansing Action*: Carbon tetrachloride is considered to be a more active and more general solvent than Stoddard solvent. It is not to be expected to remove all classes of stains, but its cleansing action is more rapid and more efficient than that of Stoddard solvent.

2—*Volatility*: Carbon tetrachloride is much more volatile than is Stoddard solvent. Fabrics cleaned in Carbon Tetrachloride will "dry" more easily and more quickly than when cleaned in Stoddard solvent.

3—*Flammability*: Carbon tetrachloride will not explode and will not burn. Stoddard solvent vapor is non-explosive only at temperatures below 105 to 110 degrees F., and Stoddard solvent is always combustible.

4—*Odor*: Carbon tetrachloride, because of its definite boiling point and greater volatility, evaporates from fabrics more rapidly than Stoddard solvent and leaves them free of solvent odor.

5—*Corrosion*: Carbon tetrachloride has a greater tendency to attack steel and some of the common metals than does Stoddard solvent. However, suitable resistant metals are available for the construction of equipment in which carbon tetrachloride is to be used.

6—*Purification*: Carbon tetrachloride can be purified by distillation much more readily, more nearly completely, and with less steam consumption than can Stoddard solvent.

7—*Health Hazard*: Because of the greater volatility of Carbon Tetrachloride dangerous concentrations of its vapor may develop more readily than dangerous concentrations of Stoddard solvent vapor. Closed systems are economically necessary, and loss of solvent vapors must be minimized. If these conditions are met and operators observe simple precautions, no health hazard need be feared.

## PAN-AMERICAN COMMERCIAL PROGRAM

(Continued from page 594)

Downright practical in application to the U. S. export dyestuffs industries are a number of the projects before the Conference in behalf of simplified or standardized trade practices. A case in point is the proposal that the Conference take definite steps to bring about uniformity in the definition of customary trade terms (such as C. I. F., etc.), especial attention to be given to those which may be ambiguous or which at present lead to confusion.

As a working basis the Conference has a mass of data assembled by chambers of commerce and similar organizations in the respective countries showing the interpretations placed upon trade terms in the different countries. To reconcile differences of interpretation and usage is the purpose of the project.

Closely allied to the effort above outlined, is the proposal that the Conference do its part to hasten inter-American commercial arbitration as a means of adjusting differences between merchants residing in different countries. A study of the situation in the American republics has revealed a lack of authority on the part of arbitrators to bring about settlement of disputes, and need of national legislation in the several countries providing for the enforcement of arbitration awards. Generally speaking, the laws of the Latin American countries or their codes of civil procedure recognize the validity of the arbitration clause as a contract itself, but if one of the parties to the dispute or misunderstanding refuses to appoint an arbitrator, there is, at present, no means by which arbitration can be enforced promptly without recourse to the courts.

Dyestuffs exporters who cultivate, or expect to cultivate, the Latin-American market will find another practical contact in the activities of the Conference looking to the favorable treatment of commercial travelers and the facilitation of the introduction of samples. Few of the national governments in the Americas levy taxes on commercial travelers, but in many cases provinces and even municipalities assess taxes which range from a mere nominal fee to three or four hundred dollars. It will be considered whether conditions might be improved by the issuance, in all countries, of cards or certificates attesting the character of credentialed travelers. The restrictions imposed upon the importation and sales of travelers' samples could be standardized to advantage. And there is need for an explicit definition of the term "a sample having no commercial value," conformity to which it has been proposed shall qualify a sample for entry free of duty.

Standardization, in one form or another, enters into many of the objectives before the Conference and in ways that touch directly or indirectly the color industries. For example, there is the proposal that the Conference outline and recommend to all the cooperating governments, uniform legislation on bills of exchange, checks and other commercial paper. Uniformity of Consular fees in the American republics and standardization of consular procedure are other submitted reforms which the Conference is counted upon to further. The need for relief in this quarter is appreciated by every shipper of dyestuffs who has fallen afoul of the diverse and involved consular regulations which handicap the flow of trade at various points in the western hemisphere.

Dyestuffs are directly involved in one continuing project which the Fourth Pan American Commercial Conference is counted upon to advance and develop. The program designation is "Standardization of commodities as an aid to commerce and for the protection of producer and consumer." This is a project which dates back to 1925 when there was held at Lima, Peru, a Pan-American Conference on Uniformity of Specifications. A second special conference was held in Washington in 1927. Wool was one of the commodities slated for attention from the outset. But it was only following the First Inter-American Conference on Agriculture, held in Washington in September, 1930, that it was agreed that dyestuffs was also one of the major commodities for which standard specifications and uniform nomenclature should be sought. An embodied responsibility is the perfecting of arrangements for the authoritative translation into Spanish of English expressions in common use in the color industries and other lines.

By no means least in importance of the dyestuffs contacts is the plan to bring before the Fourth Commercial Conference for further discussion, and possible revision, the movement for inter-American protection of trade marks and patent rights. To devise means for the inter-American protection of trade marks, inventions, industrial models, etc., that will afford adequate shelter in all countries and yet respect national legislation in each country, and involve no serious loss of national revenue anywhere, is a formidable task that may require years of negotiation. The Conference this autumn is counted upon to determine the principles that should be incorporated in whatever treaty or convention shall ultimately be provided. One of the plenary sessions of the Conference will be devoted to a discussion of the chief phases of the problem of overproduction, a subject the inter-American influences of which are exemplified by the nitrate situation in Chile and its relationship to the chemical industries in general.

## New Cloth Fabric

A method which makes it possible to produce cloth fabric closely resembling artificial silk by synthetic processes was described at the eighty-second meeting of the American Chemical Society in Buffalo.

Wallace H. Carothers and Julian W. Hill of the experimental station of E. I. du Pont de Nemours & Co. of Wilmington, Del., in reporting on the new process for the silk-resembling material, stated that their results "clearly" demonstrate for the first time the possibility of obtaining useful fibers from strictly synthetic material." The new product, they added, is shown to resemble cellulose and silk in the general plan of their molecular structure.

Hitherto the various artificial silks, such as rayon, could not be made out of "strictly synthetic material." Rayon, for example, is pure cellulose, a complicated organic product. This cellulose is turned into rayon by substituting a machine for the silk worm. The new process makes it possible for the first time to begin with simple organic substances and build up from them to the more complex ones with molecular weights from three to four times

greater than had been possible hitherto to create artificially.

The Du Pont chemists began with a compound of ethylene glycol, which is an anti-freeze mixture, and a dibasic acid which may be obtained by mixing castor oil under heat with an alkali. With this as a base, they build up a chemical substance called by them trimethylene ester of hexadecamethylene-dicarboxylic acid, which consists of carbon, hydrogen and oxygen, and is the technical name for what turns out to be a product closely resembling silk.

"The fibers so produced," it was stated, "are of good strength, pliability and high luster. The elastic properties are remarkable. Both the rate and the extent of recovery from stretch are greatly superior to viscose rayon and at least as good as silk. The luster is very brilliant and the fibers can be tied into small tight knots without breaking."

The method of preparation and the raw materials of the compounds so far studied are too costly, it was explained, to make them of any immediate practical application, but the results obtained represent a new landmark in the progress of chemistry.

### Rayon Course

Columbia University of New York City, Extension Teaching Dept., announces an evening lecture course on the manufacture, weaving and converting of rayon and other synthetic yarns and piece goods. The lectures are given by Herbert R. Mauersberger, formerly with the Celanese Corporation of America.

The lectures will begin September 24th and are held every Thursday evening from 7:30 to 9:20 P. M. The entire course consists of 15 lectures and may be repeated this spring.

The classes will be held in room 306, Mines Building on the University campus, 116th St. and Broadway. Those interested should register in room 315 University Hall, beginning September 16th, 1931. This course is open to men and women alike and is semi-technically illustrated with motion pictures, trips to nearby plants and actual samples. Persons, having to do with rayon yarns and piece goods and seeking more knowledge about this new textile material, will find the course valuable and instructive.

### Southern Textile Exposition

The tenth Southern Textile Exhibition will be held in Greenville, South Carolina, the week beginning Oct. 17, 1932.

### Vat Colors

The Roessler & Hasslacher Chemical Co., Inc., have issued a new booklet containing information on Vat colors and their oxidation.

### New Booklet

Cleaning and scouring raw wool and woven textiles with the non-inflammable Trichlorethylene is discussed in detail in the booklet "Trichlorethylene. Its Properties and Uses," recently issued by the Roessler & Hasslacher Chemical Co., Inc. Trichlorethylene, commercially known as Tri is said to be rapidly replacing older types of cleaning fluids because it has a powerful solvent action on fats, oils, and greases, is non-inflammable, is non-corrosive to metals and is harmless to textiles.

Tri is a colorless stable liquid, with a boiling point of 86.7° C. (188° F). and a density of 1.4762 at 15°/4° C. The company claims it is stable even in the presence of water at temperatures considerably above its boiling point. Its physiological action is said to be milder than that of petroleum solvents, chloroform and many other solvents according to available information.

In degreasing raw wool Tri is claimed to give good fiber cleaning, improve the appearance and durability of the wool, increase the felting properties, and prevent fire hazard. Several types of equipment are described in which Tri is employed as the cleaning solvent.

Silks and silk hosiery are said to be cleaned effectively by Tri combined with soap or sulphonated oil. The presence of the soap is said to aid materially in removing dirt as well as grease. For such woven textiles, the amount of machine oil, grease, and dirt may be from 10% to 25% by weight. A shorter cleaning time, lower power and labor costs, and a cleaner and more durable cloth are features claimed for Tri.

### Insulation

L. Mundet & Son, Inc., of Texas, cork dealers, announce that their office at Houston, Texas, has changed its location from its former address at 2420 Nance St. to their new building erected for them at Commerce and Palmer Sts., Houston. It is also announced that from this new building, with more space for carrying cork insulation of all kinds and sizes in stock, and with ample office space, better service than ever will be given to Mundet customers in the territory covered by the Houston office. In addition to carrying a complete stock of Mundet cork products this office also carries the full high temperature line of asbestos products as manufactured by Keasbey & Mattison of Ambler, Pa.

### Chemical Golf Tournament

The final golf tournament of the chemical industry will be held by the Salesmen's Association of the American Chemical Industry at Briarcliff Lodge, Briarcliff Manor, N. Y., on September 15. Several awards will be given each of the following classes: Low gross (for the good ones); low net for members (who need a handicap); low net for guests (who need a handicap); and kickers for those who are not dependable or who shoot too high a score to make effective use of a handicap. Luncheon, dinner, and entertainment in the evening are all included in the entry fee which is $10.00 for both members and guests. Entries should be directed to Grant A. Dorland, chairman of the entertainment committee, at 136 Liberty Street, New York, by noon of Monday, September 14, at the latest.

### Naphthol As-Lt

The General Dyestuff Corporation releases Naphthol As-Lt, the outstanding characteristic of which is said to be the excellent fastness to light obtainable with most Color Salts.

Especially valuable is claimed the combination with Fast Red T R Salt, giving a true Turkey Red shade of excellent all round fastness.

The company states that the next most valuable combination is with Fast Blue Salt 2 B, giving a Navy of very good fastness to light and boiling caustic.

### Du Pont Exhibit

Early fall showings of dress materials and other textiles were features during the first week of September of the Du Pont Exhibit on the Boardwalk at Atlantic City.

Women's worsted fabrics by the Hamilton Woolen Company, Inc., of Southbridge, Mass., were shown in one of the large Boardwalk windows. These woolens, sponged and pre-shrunk to 54 inch widths, were dyed with du Pont fast color dyestuffs. Patterns shown included crepe Hamilton, reversible crepe, check crepe, dotted crepe, diagonal crepe, flake tweed, reverse tweed, granite, flake check, bouclette and coating flannel. All patterns were made in a variety of thirty-four color designs.

### Cotton Goods Course

Columbia University of New York City, Extension Teaching Dept., announces a comprehensive evening course of lectures on the spinning and weaving of cotton yarns and grey goods, given by Herbert R. Mauersberger, formerly a member of Cox, Muller & Mauersberger of 320 Broadway, New York City.

The lectures will begin September 25th and are held every Friday evening from 7:30 to 9:20 P.M. The entire course consists of 15 lectures and is followed by a course in cotton goods converting in the spring.

The classes are held in room 410, Mines Building on the University campus, 116th Street and Broadway. Those interested should register at room 315, University Hall, beginning September 16th. The course is open to men and women alike and is illustrated with motion pictures, trips to nearby plants and actual samples. Persons engaged with textile concerns, seeking more knowledge about cottons, should find this course extremely valuable and instructive.


### POSITION WANTED

Color mixer and chemist, eight years' experience in printing of silk, rayon, cotton and woolen, desires connection with roller printing concern. References on request. Apply Box No. 694, American Dyestuff Reporter, 440 Fourth Avenue, New York City.

**The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.**

### DUE TO CURTAILMENT IN INDUSTRY

Textile Chemist and Colorist available for production or sales. Details and references will be furnished on request. Address Box No. 686, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.

### POSITION WANTED

Chemist — Experienced in the manufacture of sulphonated oils and textile specialty formulation. Address Box No. 688, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

### SALESMAN WANTED

A leading manufacturer of coal-tar dyes has an opening for an exceptionally able man possessing sales experience and the ability to work himself into the confidence and respect of paper mill executives. Thorough knowledge of dyes and their application to various grades of paper essential. Full details should be furnished, stating experience and present connection. All correspondence will be treated in confidence. Address Box No. 690, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.

### DYE FOREMAN WANTED

with practical experience dyeing and finishing rayon and mixed fabrics to be employed as traveling adjuster with trade. Give age, personal history, and past experience. Address Box No. 691, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.

### POSITION WANTED

DYER—Six years' experience at bleaching and dyeing wool, cotton, jute and union raw stocks and yarns. Thoroughly experienced in all stages of carpet manufacture. Age, 26; married. Address: Classified Box No. 692, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

### POSITION WANTED

Textile School graduate, North Carolina State College, B.S. degree, wishes position where he may have an opportunity to become a Chemist, Salesman or Technician. Address Box 693, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.